Hole Transport Materials for Solid-State Mesoscopic Solar Cells

LEI YANG

The solid-state mesoscopic solar cells (sMSCs) have been developed as a promising alternative technology to the conventional photovoltaics. However, the device performance suffers from the low hole-mobilities and the incomplete pore filling of the hole transport materials (HTMs) into the mesoporous electrodes. A variety of HTMs and different preparation methods have been studied to overcome these limitations. There are two types of sMSCs included in this doctoral thesis, namely solid-state dye-sensitized solar cells (sDSCs) and organometallic halide perovskite based solar cells.

Two different types of HTMs, namely the small molecule organic HTM spirom-OMeTAD and the conjugated polymer HTM P3HT, were compared in sDSCs. The photo-induced absorption spectroscopy (PIA) spectra and spectroelectrochemical data suggested that the dye-dye hole conduction occurs in the absence of HTM and appears to be of significant importance to the contribution of hole transport.

The PIA measurements and transient absorption spectroscopy (TAS) indicated that the oxidized dye was efficiently regenerated by a small molecule organic HTM TPAA due to its excellent pore filling. The conducting polymer P3HT was employed as a co-HTM to transfer the holes away from TPAA to prohibit the charge carrier recombination and to improve the hole transport.

An alternative small molecule organic HTM, MeO-TPD, was found to outperform spirom-OMeTAD in sDSCs due to its more efficient pore filling and higher hole-mobility. Moreover, an initial light soaking treatment was observed to significantly improve the device performance due to a mechanism of Li⁺ ion migration towards the TiO₂ surface.

In order to overcome the infiltration difficulty of conducting polymer HTMs, a state-of-the-art method to perform in-situ photoelectrochemical polymerization (PEP) in an aqueous micellar solution of bis-EDOT monomer was developed as an environmental-friendly alternative pathway with scale-up potential for constructing efficient sDSCs with polymer HTMs.

Three different types of HTMs, namely DEH, spirom-OMeTAD and P3HT, were used to investigate the influence of HTMs on the charge recombination in CH₃NH₂PbI₃ perovskite based sMSCs. The photovoltage decay measurements indicate that the electron lifetime (τₑ) of these devices decreases by one order of magnitude in the sequence τₑ_{spirom-OMeTAD} > τₑ_{P3HT} > τₑ_{DEH}.

**Keywords:** mesoscopic solar cells, solid-state dye-sensitized solar cells, organometallic halide perovskite, hole transport materials, mesoporous TiO₂, conjugated polymer, sensitizer, transient absorption spectroscopy, photo-induced absorption spectroscopy, in-situ photoelectrochemical polymerization, spirom-OMeTAD, P3HT, TPAA, MeO-TPD, bis-EDOT, DEH, Li⁺ ion migration, charge recombination, electron lifetime

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YANG LEI

CHINA SCHOLARSHIP COUNCIL

Presents the
2013 Chinese Government Award for Outstanding Self-financed Students Abroad
to
YANG LEI

Dr. Liu Jinghui
Secretary-General
China Scholarship Council
To my parents & family
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Comparing spiro-OMeTAD and P3HT hole conductors in efficient solid-state dye-sensitized solar cells
Lei Yang, Ute B. Cappel, Eva L. Unger, Martin Karlsson, Karl M. Karlsson, Erik Gabrielsson, Licheng Sun, Gerrit Boschloo, Anders Hagfeldt, Erik M. J. Johansson

II Combining a small hole-conductor molecule for efficient dye regeneration and a hole-conducting polymer in a solid-state dye-sensitized solar cell
Erik M. J. Johansson, Lei Yang, Erik Gabrielsson, Peter W. Lohse, Gerrit Boschloo, Licheng Sun, Anders Hagfeldt

III Initial light soaking treatment enables hole transport material to outperform spiro-OMeTAD in solid-state dye-sensitized solar cells
Lei Yang, Bo Xu, Dongqin Bi, Haining Tian, Gerrit Boschloo, Licheng Sun, Anders Hagfeldt, Erik M. J. Johansson

IV New approach for preparation of efficient solid-state dye-sensitized solar cells by photoelectrochemical polymerization in aqueous micellar solution

V Effect of different hole transport materials on recombination in CH$_3$NH$_3$PbI$_3$ perovskite sensitized mesoscopic solar cells
Dongqin Bi, Lei Yang, Gerrit Boschloo, Anders Hagfeldt, Erik M. J. Johansson

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Comments on my own Contribution
I was the main responsible person for Papers I, III and IV, for which I carried out most experimental work, data analysis and writing of the manuscripts. I performed all solar cell fabrication and characterizations, participated in data analysis and writing of the manuscript for Paper II where the transient absorption measurements were carried out by Dr. Peter W. Lohse. I was involved in the optimization of the solar cells and materials as well as in the discussion of the manuscript for Paper V. The photo-induced absorption spectroscopy and spectroelectrochemical measurements presented in Paper I were performed by Dr. Ute B. Cappel. The SEM images presented in Paper I were taken by Dr. Eva L. Unger. The hole transport material MeO-TPD employed in Paper III was synthesized by Bo Xu. The optimization of the solar cells in Paper IV was carried out by Yang Shen and Jinbao Zhang.

I am a co-author of the following papers which are not included in this thesis.

- Phenoxazine dyes in solid-state dye-sensitized solar cells
  Martin Karlsson, Lei Yang, Karl M. Karlsson, Licheng Sun, Anders Hagfeldt, Gerrit Boschloo

- Neutral, polaron and bipolaron states of PEDOT prepared by photoelectrochemical polymerization and the effect on charge generation mechanism in the solid state dye sensitized solar cell
  Byung-wook Park, Lei Yang, Erik M. J. Johansson, Nick Vlachopoulos, Amani Chams, Christian Perruchot, Mohamed Jouini, Gerrit Boschloo, Anders Hagfeldt

- Poly (3,4-ethylenedioxythiophene) hole-transporting material generated by photoelectrochemical polymerization in aqueous and organic medium for all-solid-state dye-sensitized solar cells

- Efficient and stable CH$_3$NH$_3$PbI$_3$-sensitized ZnO nanorod array solid-state solar cell
  Dongqin Bi, Gerrit Boschloo, Stefan Schwarzmüller, Lei Yang, Erik M. J. Johansson, Anders Hagfeldt
  *Nanoscale* 2013, 5, 11686-11691.
• Integration of solid-state dye-sensitized solar cell with metaloxide charge-storage material into microelectrochemical photocapacitor
  Magdalena Skunik-Nuckowska, Katarzyna Grzejszczyk, Pawel J Ku-lesza, Lei Yang, Nick Vlachopoulos, Leif Häggman, Erik Johansson, Anders Hagfeldt
  *J. Power Sources* 2013, 234, 91-99.

• Using a two-step deposition technique to prepare perovskite (CH$_3$NH$_3$PbI$_3$) for the thin film solar cells based on ZrO$_2$ and TiO$_2$ mesostructures
  Dongqin Bi, Soo-Jin Moon, Leif Häggman, Gerrit Boschloo, Lei Yang, Erik M. J. Johansson, Mohammad K. Nazeeruddin, Michael Grätzel, Anders Hagfeldt
  *RSC Adv.* 2013, 3, 18762-18766.
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<th>Full Form</th>
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<tbody>
<tr>
<td>A</td>
<td>electron acceptor in organic sensitizer or organic cation in perovskite</td>
</tr>
<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>AM</td>
<td>air mass</td>
</tr>
<tr>
<td>APCE</td>
<td>absorbed photon to current conversion efficiency</td>
</tr>
<tr>
<td>ΔA</td>
<td>change or difference in absorbance</td>
</tr>
<tr>
<td>bis-EDOT</td>
<td>2,2'-bis-(3,4-ethylenedioxy)thiophene</td>
</tr>
<tr>
<td>B</td>
<td>transition metal cation in perovskite</td>
</tr>
<tr>
<td>c</td>
<td>concentration</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
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<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>D</td>
<td>electron donor in organic sensitizer</td>
</tr>
<tr>
<td>D_0</td>
<td>diffusion coefficient of conduction band electrons</td>
</tr>
<tr>
<td>DEH</td>
<td>4-(diethylamino)-benzaldehyde diphenylhydrazone</td>
</tr>
<tr>
<td>D_n</td>
<td>chemical diffusion coefficient</td>
</tr>
<tr>
<td>DSC</td>
<td>dye-sensitized solar cell</td>
</tr>
<tr>
<td>e</td>
<td>elementary charge</td>
</tr>
<tr>
<td>E</td>
<td>electrode potential</td>
</tr>
<tr>
<td>E_0</td>
<td>flat-band potential at 0 pH</td>
</tr>
<tr>
<td>E_0-0</td>
<td>transition energy between the relaxed ground state and excited state</td>
</tr>
<tr>
<td>E_CB</td>
<td>conduction band potential</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-ethylenedioxythiophene</td>
</tr>
<tr>
<td>E_F</td>
<td>Fermi level</td>
</tr>
<tr>
<td>E_rb</td>
<td>flat-band potential</td>
</tr>
<tr>
<td>E_F,HTM</td>
<td>Fermi level in HTM</td>
</tr>
<tr>
<td>E_F,TiO_2</td>
<td>Fermi level in TiO_2</td>
</tr>
<tr>
<td>EHT</td>
<td>acceleration voltage</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>ET</td>
<td>electron transfer</td>
</tr>
<tr>
<td>Fc</td>
<td>ferrocene</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin dioxide</td>
</tr>
</tbody>
</table>
spirobifluorene
SCLC space charge limited current
sDSC solid-state dye-sensitized solar cell
SEM scanning electron microscopy
SHE standard hydrogen electrode
sMSC solid-state mesoscopic solar cell
t time or tolerance factor
\(t\)-BP 4-\(\text{tert}\)-butylpyridine
\(T\) temperature or transmittance
TAS transient absorption spectroscopy
\(T_g\) glass transition temperature
\(T_m\) melting point
TPAA tris(\text{para-}anisyl)amine
\(V\) voltage
VB valence band
\(V_{\text{max}}\) voltage at maximum power point
\(V_{\text{oc}}\) open circuit voltage
\(\Delta V\) change or difference in voltage
WD working distance
WE working electrode
\(X\) anion in perovskite
XPS X-ray photoelectron spectroscopy
\(\varepsilon_0\) permittivity of the vacuum
\(\varepsilon_r\) dielectric constant
\(\varepsilon(\lambda)\) extinction coefficient
\(\eta\) power conversion efficiency
\(\lambda\) wavelength
\(\mu\) mobility or octahedral factor
\(\pi\) conjugated linker in organic sensitizer
\(\sigma\) conductivity
\(\tau_0\) lifetime of conduction band electrons
\(\tau_n\) electron lifetime
\(\tau_{\text{resp}}\) response time of photocurrent decay
\(\tau_{\text{trans}}\) electron transport time
\(\phi_{\text{cc}}\) charge collecting efficiency
\(\phi_{\text{inj}}\) injection efficiency
\(\phi_{\text{reg}}\) regeneration efficiency
\(\Phi\) photon flux
1. Introduction

1.1 Solar energy

Energy and environment have become two of the most concerned topics in the 21st century. Mankind’s civilization has achieved great success in modern industries at the cost of foreseen depletion of non-renewable energy sources and irreversible climate change, which have induced a variety of obstacles against sustainable development for the future generations. The total global energy consumption has been increasing rapidly over decades eventually reaching a striking record of 8919 Mtoe (million tonnes of oil equivalent) in the year of 2011. However the usage of non-renewable energy sources still accounts for the major portion of the energy production approximately by 66.4% including crude oil, coal and natural gas. Meanwhile burning fossil fuels has caused certain irreversible environmental damages, such as air pollution and global warming. To cope with these challenges, the research into renewable energy technologies therefore becomes the key to the sustainable future. In general, renewable energy sources consist of solar radiation, wind, hydropower, tides, biomass and geothermal heat. Combining the non-renewable and the renewable energy sources has already become the most feasible solution in the business of global electricity production by the end of 2013 (Figure 1.1), where the hydropower comprises the greatest share of 16.4% and solar photovoltaics accounts for their latest record of 0.7% share of total renewable electricity production with an average increasing rate of 60% annually.

Figure 1.1: Estimated renewable energy share of global electricity production, End-2013. The renewable energy accounts for 22.2% of the global electricity production where the solar PV contributes 0.7% to the renewable electricity production at the end of 2013.
Solar energy is considered as the only inexhaustible renewable source with large potential on the earth as the sun provides approximately $1.7 \cdot 10^5$ TW of the electromagnetic radiation striking the earth’s atmosphere, practically providing around 600 TW global terrestrial solar energy when around 30% reflection by earth’s atmosphere is taken into account. In comparison, the annual global electricity consumption in 2011 was estimated as 19298.5 TWh indicating the average power consumption of around 2.2 TW. The solar energy received on the earth’s surface is therefore significantly beyond being capable of fully covering the electricity demand around the globe.

![Figure 1.2: The standard normalized solar spectrum and the corresponding solar photon flux distribution on the earth’s surface with the irradiance normalized to an integrated power density of 1000 Wm$^{-2}$ (AM 1.5 G).](image)

The spectrum of solar irradiance appears similar as that of black body radiation at a temperature of 5800 K. Based on the duality principle, the solar irradiance is highly influenced by the earth’s atmosphere (e.g. reflection and absorption) along the pathway before arriving at the earth’s surface. The spectrum depends on the path length of photons with different energies through the earth’s atmosphere, which eventually appears as a spectrum of irradiance distribution correlated to photon energies. Figure 1.2 shows the terrestrial solar spectral irradiance and the corresponding solar photon flux $\Phi(\lambda)$ distribution as functions of the electromagnetic wavelength at the air mass of 1.5 (AM 1.5 G). This is the most widely used standard solar spectrum with the irradiance normalized to an integrated power density of 1000 Wm$^{-2}$ for the purpose of calibrating and characterizing solar cells. The UV-visible (ultra-violet and visible irradiance roughly designates the spectral region from 280 to 780 nm) and near infra-red (near-IR irradiance roughly denotes the spectral region from 780 to 1400 nm) spectral regions cover the most solar spectrum and photon flux distributions. Therefore the combination of these two spectral regions includes the optimal absorption region for a solar cell device.
As an emerging renewable energy technology, solar cells (or photovoltaics, PV) have shown great potential with remarkably rapid growth during the last decade. Until the beginning of 2014 a total capacity of 139 GW had been installed around the globe. In spite of the large growth of solar PV installation the challenge of minimizing payback time and fabrication cost still remains to be conquered. In order to provide sufficient contribution to the gross global electricity production with sustainable development strategy, more and more high-efficiency, cost-effective, recyclable and environmentally-friendly solar cell systems need to be developed in future.5

1.2 Overview of photovoltaic technologies

1.2.1 Inorganic solar cells

The first experimental demonstration of the photovoltaic effect by Edmond Becquerel, a French scientist, opened the research field of photovoltaics in 1839. Although the first solid-state photovoltaic device with merely around 1% power conversion efficiency (η) was fabricated by Charles Fritts with a charge separation junction formed by semiconductor selenium coated with a thin layer of gold (Au) in 1883, the insight on how the solar cell device worked still remained poorly understood for more than half century until that the fundamental interpretation for the mechanism of photoelectric effect was proposed in 1905 by Albert Einstein to explain the photo-induced charge carrier excitation process, for which Einstein was eventually awarded the Nobel Prize in Physics in 1921. Based on the knowledge acquired from the research on transistors, scientists in Bell laboratory, Daryl Chapin, Calvin Fuller and Gerald Pearson, successfully developed the first practical silicon photovoltaic device (normally referred as 1st generation solar cell) in 1954 after the Second World War, as a breakthrough which at the first time proved that the photovoltaic cell based on semiconductor material silicon showed remarkable potential of converting solar irradiance into electricity with around 6% efficiency.6 However, due to the high production cost and low energy conversion efficiency after the improvements over two decades the initial application of this type of photovoltaics only appeared in space research field as equipped on the outside surface of satellite or as large wing-shaped solar panels providing electricity support for spacecraft without modifying the power system.

The photo-induced charge separation in silicon solar cell is typically based on the built-in electric potential across the doped silicon p-n junction (Figure 1.3). Due to the narrow band gap and low absorption coefficient of silicon these solar cells usually require a relatively thick absorption layer (typically more than 100 μm) grown from high-purity grade of silicon with precisely controlled doping levels. Therefore the fabrication of silicon solar cells is
Considerably energy intensive with significant costs in spite of the fact that silicon is one of the most abundant elements. Over decades the fabrication cost of silicon solar cells has been reduced sufficiently for civil applications due to the progressive improvements in processing technology by semiconductor manufacturing industry. At present 20-25% power conversion efficiencies for crystalline silicon and up to around 10% for amorphous silicon are achieved with reasonable production costs.  

![Figure 1.3: Schematic structure and working mechanism of a p-n junction based silicon solar cell, where the antireflection film is employed to increase the light harvesting by reducing the reflection on the substrate surface.](image)

Analogous to silicon cells, in most inorganic solar cells using semiconductor materials charge separation occurs at the p-n junction. The difference mainly lies in the intrinsic photovoltaic properties of the materials, such as higher absorption coefficient and wider band gap. Apart from silicon a variety of semiconductor materials have been investigated and successfully used to produce high-efficiency solar cells, such as 19.6% for CdTe, 23.3% for CuInGaSe$_2$ (CIGS), 28.8% for GaAs. However, all these types of inorganic solar cells require high purity grade of the semiconductor materials in use for achieving high power conversion efficiencies. Thus, the research into cost-effective solar cells with accessible and affordable materials needs to proceed.

1.2.2 Organic solar cells

Photovoltaics based on organic semiconductor materials have attracted intense attention since the first organic solar cell with power conversion efficiency of 1% was fabricated using a combination of electron donor (D) and acceptor (A) organic semiconductors. Unlike the rigid structure of inorganic solar cells, organic photovoltaics (OPV) provide not only the possibility of structuring flexible devices with relatively low cost but also the technical solutions for up-scalable roll-to-roll production of solar cell devices. At present this type of devices can be already found popular in applications such as buildings and electronic consumer products, which are partially covered by
flexible organic solar cells with low efficiencies as complementary power supply.

Despite the great success in the PV market, the operating mechanism of OPV still remains incompletely understood. Similar to inorganic solar cells, it is believed that upon photo-excitation, the excited state of the light harvesting material, termed as exciton (coupled electron-hole pair), is formed with a certain lifetime. The thermodynamic offset is required to overcome the exciton binding energy to create free charge carriers (uncoupled electron and hole) at the junction interface between light harvesting electron donor (p-type) and acceptor (n-type) materials. However, the exciton binding energy in OPV is usually much greater than that in the inorganic cells. Therefore the thermodynamic driving force for interfacial charge separation and the exciton diffusion length become the limiting factors for the photovoltaic performance of OPV devices.

Figure 1.4: Schematic operating mechanism of organic solar cell based on polymer materials, where P3HT is a p-type polymer functioning as the light harvesting electron donor and PCBM is a n-type fullerene derivative working as the electron acceptor. After diffusion, the exciton is dissociated into free charge carriers at the junction interface between electron donor (p-type) and acceptor (n-type) materials.

For optimal light harvesting, an adequately thick absorbing layer is needed, which however increases the exciton diffusion pathway to the donor/acceptor interface. The advanced design of bulk-heterojunction OPV solved such a bottleneck by depositing a mixture of the electron donor and acceptor materials as a bulk-heterojunction layer. This approach minimizes the exciton diffusion pathway meanwhile ensures sufficient light absorption volume, which significantly improved the efficiency of separating exciton into free charge carriers and eventually increased the power conversion efficiency. However, the phase-separation processes on the microscopic scale after the formation of co-deposited bulk-heterojunction layer becomes the new primary limiting factor to the further improvement of photovoltaic performance for this type of solar cells.
As illustrated in Figure 1.4, a mixture of poly(3-hexylthiophene-2,5-diyl) termed as P3HT (p-type polymer functioning as the electron donor) and [6,6]-phenyl C61 butyric acid methyl ester termed as PCBM (n-type fullerene derivative working as the electron acceptor) is deposited to form the bulk-heterojunction layer where the exciton is created upon photo-excitation and dissociated at the electron donor/acceptor (P3HT/PCBM) interface. The performance of this device is partly determined by the phase-separation morphology of the co-deposited P3HT/PCBM layer. So far, the company Mitsubishi Chemicals holds the world record efficiency of 11.1% for organic solar cells, which is a promising value for such an emerging technology with great industrial potential.

1.2.3 Dye-sensitized solar cells

The concept dye-sensitization was initially introduced by Moser in 1887 with an experimental demonstration showing that photocurrent was slightly enhanced by dye-sensitizing halogenated silver (Ag) plates. However, academic attention and research interest were unfortunately not attracted by such an interesting discovery until the first underlying operating mechanism was proposed in 1976 to interpret how this type of device performs light harvesting and charge separation. More and more intensive research into dye-sensitized solar cells (DSCs) has been carried out since a low-cost photoelectrochemical cell with 7% power conversion efficiency was demonstrated by O’ Regan and Grätzel in 1991. The breakthrough in terms of efficiency is attributed to the combination of the mesoporous titanium dioxide (TiO$_2$) used as photoanode material and the electrolyte containing iodide/triiodide redox shuttle. The design using mesoporous TiO$_2$ with a large surface area completely deviates from the conventional understanding suggesting that a large interfacial surface area must be averted in solar cell devices in order to efficiently suppress recombination between free charge carriers. However, the fast electron transport through the TiO$_2$ anode and slow charge recombination kinetics at the interface between $I^-/I_3^-$ redox couple and photoanode coincidently allow the device to function efficiently featuring large surface area for remarkably enhanced light absorption.

Dye-sensitized solar cells are fabricated mostly with abundant and affordable materials, which are usually cost-effective and environmental-friendly. As shown in Figure 1.5, a wide band gap n-type semiconductor material, anatase TiO$_2$ nanoparticles (generally around 20 nm in diameter) are deposited and interconnected on fluorine-doped tin dioxide FTO (F:SnO$_2$) coated conducting glass as photoanode, which is attached by dye molecules (sensitizers). The electronic transition occurs upon light absorption in the sensitizers, which leads to the formation of an excited state of the dye (exciton). Compared with inorganic or organic solar cells, in DSC charge separation occurs at the interface by excited dye injecting photo-induced electrons into the conduction band (CB) of mesoporous TiO$_2$ working electrode. This sig-
nificantly eliminates the loss of charge collecting efficiency ($\varphi_{cc}$) caused by the recombination along their diffusion pathway. The injected electrons are afterwards transported through the interconnected mesoporous TiO$_2$ network towards the FTO substrate of photoanode described by a diffusion controlled trapping-detrapping dynamic theory.$^{18,19}$ After electron injection, the dye molecule in its oxidized form is subsequently regenerated by electron donation from the electrolyte containing I$_3^-$/I$_{-}^-$ redox couple dissolved in organic solvent, normally acetonitrile (MeCN). Meanwhile the holes are transferred via the redox couple towards the platinized FTO counter-electrode (CE) to complete the circuit.$^{20,21}$ Marcus theory suggests that the kinetics of an electron transfer process is determined by the driving force, the difference in free energy, and the electronic coupling between the two transition states. The operating mechanism of DSCs can also be described by several electron transfer (ET) reactions with certain rate constant in cooperation, which need to be coordinated in the right order, namely in desirable kinetic rates, by tuning and matching the electronic states of the DSC components in order to build a functioning device.$^{22}$

Figure 1.5: Schematic operating mechanism of liquid-electrolyte dye-sensitized solar cell based on mesoporous TiO$_2$ photoanode and I$^-$/I$_3^-$ redox couple.

The output voltage of a DSC device is determined by the energy difference between the redox potential of the electrolyte and the electron quasi-Fermi level ($E_F$) in the TiO$_2$ under working conditions. The photocurrent output depends on the absorption spectrum of the dye and the absorbed photon to current conversion efficiency (APCE), also known as the internal quantum efficiency (IQE). During the past two decades a variety of research efforts have been devoted into the improvement of photovoltaic performance of DSCs$^{23-26}$ including: designing the dye families with higher extinction coefficients $\varepsilon(\lambda)$ and wider absorption spectral range;$^{27-31}$ investigating alternative
redox shuttles with better capability of recombination prohibition and one-electron transfer mechanism for lower loss in regeneration energy driving force;\textsuperscript{32-37} seeking more cost-effective and stable semiconductor materials as photoanode and tuning the interfacial morphology to achieve higher surface area and faster electron transport properties;\textsuperscript{38-45} searching better materials to replace the platinized FTO counter-electrode in terms of up-scalable production of DSC devices.\textsuperscript{46,47} Eventually the world record power conversion efficiency of 13\% has been achieved by Grätzel et al. in 2014 for the liquid electrolyte based DSCs.\textsuperscript{31}

Although liquid electrolyte based DSCs have shown promising potential as alternative photovoltaic devices to conventional solar cells some limitations still remain to be solved to further improve this type of devices. In order to efficiently suppress the interfacial recombination between free electrons in the TiO$_2$ and the redox shuttle the excessive amount of triiodide with high concentration is commonly used in the electrolyte, being fairly corrosive with high possibility of eroding the capsulation layer of the device. In addition the electrolyte commonly used in the high-efficiency liquid DSCs consists of polar organic solvents with high dielectric constant to guarantee fast transport of redox shuttle such as MeCN, which is highly volatile and readily evaporates away through the joint device cross-section leading to a leakage problem of the electrolyte in the complete devices even with sealing technologies applied. Such a flaw causes the gradual efficiency degradation and therefore significantly restricts the industrial application of DSCs in terms of long-term stability. Moreover, the over-potential between the redox potential of I$^-$/I$_3^-$ mediator and the highest occupied molecular orbital (HOMO) level of the dye (the regeneration potential of dye/dye$^+$) accounts for the part of the major energy losses in the output photovoltage as the redox potential of redox couple needs to be minimized until the sufficient energy driving force remains for the efficient regeneration of the dye molecules in their oxidized form.\textsuperscript{48} The problems discussed above became the primary driving force for the development of solid-state dye-sensitized solar cell (sDSC), one type of solid-state mesoscopic solar cells (sMSCs), to replace the electrolyte with a solid-state semiconductor as hole transport material (HTM). In 1998, Bach et al. successfully demonstrated the first sDSC by employing a small organic molecular p-type semiconductor as HTM replacing the conventional electrolyte, namely 2,2’,7,7’-tetrakis(N,N-dimethoxyphenylamine)-9,9’-spirobifluorene, termed as spiro-OMeTAD (Figure 1.6).\textsuperscript{49} Since then intensive research effort has been devoted into sDSC research field. The efficiency of sDSC using spiro-OMeTAD as HTM has been improved remarkably to 6.08\% of a certified device in association with a custom-synthesized dye,\textsuperscript{50} and to 7.2\% in the Grätzel group by addition of small portion of a cobalt complex as p-type dopant.\textsuperscript{51}
However, the intrinsic properties of spiro-OMeTAD become the limitation factors for the improvement of the relatively low efficiency of sDSCs compared to liquid electrolyte DSCs, such as low hole-mobility, fast interfacial recombination rate and insufficient infiltration into the mesoporous photoanode. To overcome these shortages of spiro-OMeTAD, other types of HTMs have also been tested for the development of sDSCs. Small molecule organic HTMs with competitively low synthetic cost and high hole-mobility have been designed and investigated to improve the hole-conduction and infiltration, however these devices are still less efficient than those based on spiro-OMeTAD due to the higher recombination of charge carriers at the interface between TiO$_2$ and HTMs. Based on the knowledge gained from the OPV field conjugated p-type polymers with high conductivity and possible contribution to photocurrent have been tested as HTMs in sDSCs as well, such as P3HT (Figure 1.6). However, the efficiencies of these devices remain much lower as the result of incomplete HTM infiltration due to the low solubility of HTMs during the solution-processed device fabrication. In order to further improve the infiltration of conjugated polymer into the pores of mesoporous oxide electrode, a technique termed as in-situ photoelectrochemical polymerization (PEP) has been developed. In this approach small organic precursors corresponding to the resulting conjugated polymer, typically poly(3,4-ethylenedioxythiophene) termed as PEDOT, is dissolved in solution and located in direct contact with the dye, therefore the photo-induced polymerization takes place directly inside the pores to circumvent infiltration problem. So far the promising record efficiency of 7.1% has been achieved for this type of sDSCs based on conjugated polymer produced by in-situ PEP.

### 1.2.4 Perovskite based solar cells

Based on the knowledge of organometallic halide perovskites acquired in light-emitting diode and transistor research fields, the idea of using or-
ganometallic lead halide perovskites as light absorber in electrolyte based photoelectrochemical cells was initially introduced by Miyasaka et al. in 2009 with a power conversion efficiency of 3.8%. In terms of structure such a system suffers from fast degradation due to the dissolution of perovskite absorber into the organic electrolyte even though an efficiency of 6.5% was obtained by improvement. However, by replacing the electrolyte with the solid-state p-type semiconductor spiro-OMeTAD a significant improvement of 9.7% efficiency was achieved by Park et al. in 2012. In approximately the same time, Snaith et al. successfully demonstrated that the TiO₂ photoanode can be replaced by a Al₂O₃ mesoporous scaffold with a competitively high efficiency of 10.9% in such an organometallic lead halide perovskite based solid-state mesoscopic solar cell.

The most commonly used lead halide perovskites in MSCs are formulated as CH₃NH₃PbI₃ and CH₃NH₃PbI₃₋ₓClₓ due to the difference in the preparation methods. The operating mechanism of perovskite based MSCs using mesoporous TiO₂ as photoanode is similar to that of sDSCs, where the perovskite functions as light harvesting component absorbing incident light followed by the injection of photo-electrons into the conduction band of TiO₂ semiconductor. While the perovskite based MSCs with the Al₂O₃ mesoporous scaffold operate in a slightly different way that no electron injection occurs after photo-excitation as the conduction band of Al₂O₃ is higher with regard to the excited state of the lead halide perovskite. This indicates that apart from absorbing photons the exciton diffusion or dissociation is also accomplished in the perovskite layer due to the sufficiently long electron-hole diffusion length.

However, in spite of the distinct operating mechanisms both types of perovskite based MSCs exhibit considerably high photocurrent compared to sDSCs, which is mainly attributed to the powerful light harvesting capability. The absorption coefficient of lead halide perovskite is measured to be one order of magnitude higher than organic dyes, and the absorption spectrum of lead halide perovskite appears to be remarkably broad covering the entire visible region and partially the near-IR range. In addition the open circuit voltage (V_{oc}) of perovskite based MSCs is recently found mainly depending on the energy difference between the HOMO level of HTMs and the electron quasi-Fermi level in the perovskite absorber materials rather than that in the semiconductor materials of the photoanode. The high electron quasi-Fermi level in perovskite absorbers at open circuit condition explains the reason why perovskite based MSCs normally exhibit relatively high V_{oc} exceeding 1 V.

In terms of modifying the molecular formula and structure such as substitution of transition metals and changing the halide composition, the high tunability of metal halide perovskites provides a variety of possibilities to improve the photovoltaic performance of perovskite based MSCs. So far an impressive world record efficiency of 17.9% has been certified for this type of solar cells.
1.3 Aim of the thesis

The aim of this doctoral thesis is to investigate the working principles of different hole transport materials in solid-state mesoscopic solar cells in order to further understand these devices and eventually to improve their photovoltaic performance. There are two types of sMSCs included in this study, namely solid-state dye-sensitized solar cell and organometallic halide perovskite based solar cell. The investigation was initially focused on increasing the further understanding of the fundamental operating mechanisms to identify the limiting factors in these devices. A variety of HTMs and different preparation methods have been studied in order to circumvent these device limitations.

By comparing p-type conjugated polymers with small molecule organic p-type semiconductors functioning as HTMs in sDSC, the hole diffusion via hopping through the monolayer of sensitizers was observed to significantly contribute to the hole transport. Moreover, the photo-induced absorption spectroscopy (PIA) was performed in association with scanning electron microscopy (SEM) to investigate the influence of the HTMs with different pore filling on regeneration efficiency (Paper I). The regeneration of oxidized dye was found to be highly efficient by employing a small molecule organic HTM with expected high pore filling suggested by PIA measurements. The device, however, exhibited low performance suffering from the fast charge recombination at the HTM/TiO$_2$ interface. The laser-induced transient absorption spectroscopy (TAS) indicates that the charge recombination was prohibited efficiently and the hole conduction was facilitated significantly by addition of a conjugated polymer as co-HTM (Paper II). A mechanism of device performance evolution depending on Li$^+$ ion migration towards the surface of TiO$_2$ nanoparticles was suggested to interpret the effect of efficiency evolution under light soaking observed when high performance of sDSC was obtained by using an alternative small organic HTM with higher hole-mobility and pore filling compared to spiro-OMeTAD (Paper III). In order to cope with the difficulty of a conjugated polymer to thoroughly infiltrate the mesoporous TiO$_2$ electrode, a state-of-the-art approach, in-situ photoelectrochemical polymerization, was utilized to produce PEDOT as HTM directly inside the pores of photoanode (Paper IV). The influence between different types of HTMs on charge recombination in the CH$_3$NH$_3$PbI$_3$ perovskite based sMSC devices was studied in terms of regeneration efficiency and electron lifetime by using PIA and photovoltage decay measurements (Paper V).

As a prospect for future work and a summary of the results to facilitate reading the papers, the following chapters are outlined below:

- Chapter 2 identifies the problems and limitations in sMSC based on the thorough discussion of each component and the comprehensive analysis of the electron transfer reactions occurring at the interfaces.
Chapter 3 introduces the diversity of different types of HTMs in terms of their distinct physical properties and synthetic approaches. Subsequently the insights on how the electronic properties of these HTMs influence the photovoltaic performance in sMSC devices are discussed.

Chapter 4 specifies the methodology of sMSC device fabrications followed by the introduction of the advanced techniques for characterizing the component materials and the complete devices.

Chapter 5 presents the most important findings observed and knowledge acquired with regard to the influence of different HTMs on sMSC device performance during the PhD study presented in the five publications included in this thesis.

Chapter 6 summarizes the implications of the obtained results with conclusions for the development of sMSCs providing a blueprint for the future work.
2. Mesoscopic solar cells

The mesoscopic solar cells involved in this thesis study includes solid-state dye-sensitized solar cell and organometallic halide perovskite based solar cell. In terms of device structure, these two types of sMSCs are usually constructed in a highly similar way consisting of five major components: the working electrode made of metal oxide also termed as photoanode designed with the morphology of high surface area; the light absorbing material, such as dye molecules, light absorbing polymer and organometallic halide perovskite; the hole transport materials; additives employed to pre-oxidize hole transport materials to facilitate hole conduction and to modify the energy alignment or properties of the interfaces; the counter-electrode. The photovoltaic performance of the sMSC devices is dominated by not only the properties of each component but also how efficient they corporate with one another; “the marriage of materials is important” said Michael Grätzel, the father of dye-sensitized solar cell. This chapter introduces the properties of the materials used for each component, subsequently discusses how these components influence the photovoltaic performance in sMSCs based on the fundamental understanding of the operating mechanism in terms of electron transfer reaction and the transport of charge carriers, and eventually recognizes the problems and limitations occurring in the devices as a guideline for further improvement of sMSCs.

2.1 Solid-state dye-sensitized solar cells

2.1.1 The working electrode

The commonly used substrate for working electrodes in sDSCs is optical glass coated with a transparent conducting metal oxide, such as tin-doped indium oxide (ITO) or FTO featuring the high transparency, the low reflection and absorption, the low sheet resistance and the high thermal stability. All substrates used in the sDSCs involved in this thesis work are high-transparency FTO-coated glass purchased from Pilkington with the sheet resistance of 15 Ω/□ and the thickness of 2.3 mm. The materials of working electrode active layer in the sDSCs are normally the n-type metal oxide semiconductors, such as TiO₂, zinc oxide (ZnO) and tin dioxide (SnO₂). There are three crystal structures of TiO₂ that have been intensively studied, name-
ly the rutile, the brookite and the anatase. Although the TiO\(_2\) with rutile and brookite crystal structures are thermodynamically more stable than that in anatase crystal form, anatase TiO\(_2\) with a wide band gap transition energy of 3.2 eV is most commonly used as the working electrode material in sDSCs. According to a sol-gel synthetic scheme with high yield, colloidal nanoparticles of anatase TiO\(_2\) are produced in diameter of 20 nm approximately with a flat-band potential (E\(_{fb}\)) calculated by the Equation 2.1 as below,\(^7^3\), which is around 40 mV less negative than the value obtained for the TiO\(_2\) mesoporous electrode (Equation 2.2).\(^7^4,^7^5\)

\[
E_{fb(\text{nannoparticle})} = -(0.12 \pm 0.02) - 0.059 \text{ pH V (vs. NHE)} \quad (2.1)
\]

\[
E_{fb(WE)} = -0.4 - 0.06 \text{ pH V (vs. SCE)} \quad (2.2)
\]

The flat-band potential at 0 pH (E\(_0\)) is normally calculated from Mott-Schottky plot determined by Mott-Schottky Equation (2.3, valid for dense semiconductor electrodes rather than mesoporous electrodes),\(^7^6\) where C is the capacitance, E denotes the electrode potential, E\(_{fb}\) designates the flat-band potential, \(k_B\) is the Boltzmann constant, T is the temperature, e is the electron charge, \(\varepsilon_0\) is the permittivity of the vacuum, \(\varepsilon_r\) is the dielectric constant, and \(N_D\) is the donor density. Since the flat-band potential is a qualified approximation of the electron quasi-Fermi level in the n-type semiconductor, the E\(_{fb}\) value therefore indicates roughly where the conduction band edge potential lies in the energy diagram.

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 \varepsilon_r N_D} \left( E - E_{fb} - \frac{k_B T}{e} \right) \quad (2.3)
\]

The pre-cleaned FTO glass substrate is coated by a dense layer of TiO\(_2\) as hole blocking layer before the preparation of mesoporous TiO\(_2\) layer in order to restrict the charge carrier recombination. In the absence of the dense TiO\(_2\) blocking layer, the FTO remains partially exposed in direct contact with the HTMs due to the fact that the mesoporous electrode covers the FTO surface incompletely by the interconnected nanoparticle network, even with the surface modification by dye molecules. This significantly shunts the solar cell as the result of an enhanced dark current generated by the recombination at the HTM/FTO interface through the cross-section of photo-anode all the way to the counter-electrode when the device is under illumination at working condition, particularly the \(V_{oc}\) deceases dramatically due to the depletion of injected photo-induced electrons by recombination with the holes located in the HTM layer when the device operates at open circuit condition. It is experimentally proven that large dark current through the heterojunction of sDSC based on spiro-OMeTAD as HTM severely harms the photovoltaic performance of the devices due to the fast charge recombination between FTO and spiro-OMeTAD rather than any other recombination reactions.\(^7^7\)
Thus, the dense layer of TiO$_2$ with minimized amount of pinholes is necessary to suppress recombination in sDSCs. The method of spray pyrolysis deposition was further developed and used to produce TiO$_2$ blocking layers in the sDSC devices involved in this study.$^{78}$ In this approach, a precursor solution containing titanium (IV) acetylacetonate is sprayed onto the preheated surface of FTO substrate at around 450 °C to form a dense layer of crystalline TiO$_2$ by high temperature pyrolysis reaction. In order to completely avoid the presence of pinholes, the thickness around 250 nm of the blocking layer was found to be sufficient by designed experiments as shown in Figure 2.1 (a), where the sDSC device exhibits 4.7% efficiency using D35 as sensitizer and spiro-OMeTAD as HTM.

In order to provide a large surface area, the colloidal nanoparticles of anatase TiO$_2$ are coated onto the dense blocking layer to form a mesoporous scaffold layer for anchoring light absorbers, dye molecules. There are three commonly used methods to deposit the mesoporous layer, such as doctor-blading, screen-printing and spin-coating, where the first two are usually employed to form a thick layer in the range from 5 to 30 μm and the last one is mainly used to generate a low thickness of around 1 to 5 μm based on the viscosity of the TiO$_2$ colloidal paste in use. Due to the infiltration and recombination limitation of most HTM based devices, the optimized film thickness of the mesoporous layer is normally found to be around 2.3 μm in sDSC devices. Therefore spin-coating becomes the mostly used method to prepare the TiO$_2$ mesoporous scaffold in sDSCs due to its high reproducibility and tunability. By tuning the viscosity of the TiO$_2$ paste and the spin-coating procedure, different film thickness can be achieved.

![Figure 2.1: Scanning electron microscopy images of a sDSC device using D35 as sensitizer and spiro-OMeTAD as HTM. The entire cross-section of the device consists of FTO glass conducting substrate, electron blocking layer of dense TiO$_2$, D35 sensitized mesoporous TiO$_2$ network filled with spiro-OMeTAD and the Ag counter-electrode (a, left). The magnification of the mesoporous TiO$_2$ electrode layer (b, right).](image)

As shown in Figure 2.1, the TiO$_2$ mesoporous scaffold with a thickness of around 2.3 μm is deposited onto the blocking layer coated FTO substrate by spin-coating technique from a colloidal nanoparticle paste with diluted con-
centration. The formed TiO\(_2\) film is subsequently sintered on the hotplate at 450 °C for 30 minutes. During this process, the solvents and additives in the diluted TiO\(_2\) paste evaporate away to interconnect the nanoparticles into the mesoporous network, and the phase transition processes ensure that all any other crystal structures of TiO\(_2\) are transformed into anatase phase. The TiO\(_2\) mesoporous scaffold prepared in this manner usually provides a large surface area with a high roughness factor of around 1000.\(^{23}\) Figure 2.1 (b) clearly shows that the mesoporous TiO\(_2\) scaffold after sintering provides a large density of pores with high roughness, which remarkably increases the dye loading of the sensitizers (the amount of the dye attached) onto the TiO\(_2\) surface of the photoanode to facilitate more efficient light harvesting. The roughness and pore size of the mesoporous film can be readily tuned by the original size of the TiO\(_2\) nanoparticles and the additive concentration used in the diluted paste prior to spin-coating, which are the most important factors in terms of dye loading and infiltration of HTMs. However, the balance between these two factors needs to be compromised within a given film thickness, which suggests a optimized combination for high-efficiency sDSCs with 20 nm TiO\(_2\) particle size and 2.3 μm film thickness.

After sintering, the surface of the mesoporous TiO\(_2\) film is modified with a TiCl\(_4\) treatment, which is performed by immersing the sintered mesoporous film into the TiCl\(_4\) aqueous solution normally with heating for certain time. Such a treatment is believed to further improve the interconnection between TiO\(_2\) nanoparticles by creating a fine layer of TiO\(_2\) between the surfaces of the nanoparticles. The TiCl\(_4\) treatment was found to increase the short circuit current (\(I_{sc}\)) by improving the electron transport through the TiO\(_2\) mesoporous network and suppressing the charge recombination at interfaces.\(^{80,81}\) As one of the most crucial procedures influencing the photovoltaic performance, the TiCl\(_4\) treatment is therefore adopted as a routine step in the fabrication process of the sDSC devices based on mesoporous TiO\(_2\) photoanode.

2.1.2 The sensitizing dyes

As light harvesting component, sensitizing dye molecules are anchored onto the surface of the working electrode since the most semiconductor materials used for working electrode exhibit no absorption in the visible spectral region due to their large band gaps. A variety of different families of dyes have been designed and synthesized for improving the light harvesting in sDSC devices, which includes two major categories: the organometallic and organic dyes. In the early stage, a number of organometallic sensitizers based on ruthenium (Ru) complex have been intensively studied and developed for liquid electrolyte DSCs due to their high thermal stability and facile syntheses, such as ruthenium dyes coded as N719, Z907 and N3.\(^{27-29}\) However, the thickness of working electrodes of the sDSCs using ruthenium sensitizers in general needs to be relatively high in order to absorb sufficient light since the extinction coefficients of most ruthenium dyes are fairly low. Therefore
the research of developing organic sensitizers has attracted intensive attention due to their unique advantages compared to ruthenium sensitizers. The electronic properties of organic dyes can be readily tuned by modifying their molecular structures. In particular the majority of organic dyes exhibit higher extinction coefficients than ruthenium complexes, and the organic dyes can be further optimized by structural modification. For instance, the organic dye coded as LEG4 (Figure 2.2) used in the study of Paper III exhibits a maximal extinction coefficient of $4.9 \cdot 10^4 \text{M}^{-1}\text{cm}^{-1}$, which is four times greater than that of the ruthenium sensitizer Z907 (Figure 2.2), $1.2 \cdot 10^4 \text{M}^{-1}\text{cm}^{-1}$, used in the study of Paper IV.

According to the sDSC operating mechanism and the research of dye development, a series of criteria needs to be fulfilled for a sensitizing dye to successfully function in the sDSC devices. The dye ought to exhibit high extinction coefficient with absorption spectrum covering as much spectral region as possible since the light harvesting efficiency (LHE) of the sDSC device is derived from the absorbance $(A(\lambda))$ of the dye-sensitized TiO$_2$ electrode, expressed in the following equation:

$$LHE = 1 - 10^{-A(\lambda)}$$  \hspace{1cm} (2.4)

Therefore the LHE of a sDSC device is generally determined by four factors including the extinction coefficient of the dye, the width of the absorption spectrum of the dye, the mesoporous film thickness and the dye loading on the film. In addition, the lowest energy level of the excited state of dye (related to the lowest unoccupied molecular orbital (LUMO)) ought to be higher than the energy of the TiO$_2$ conduction band edge with sufficient driving force for electron injection. The excited state of dye ought to last long enough without decay before the electron injection takes place, which means that the lifetime of excited state ought to be long enough to allow the electron injection to occur. The HOMO energy level of the dye ought to be less negative with respect to that of HTMs for sufficient regeneration driving force. In terms of stability, the dye ought to be thermally and electrochemically stable for functioning at working conditions of sDSCs. The electrochemical properties of the dyes used in this thesis work are specified in Table 2.1 with their absorption characteristics as well, such as the $E_{0-0}$ transition energy (the energy of the electronic transition between the lowest vibrational state of the ground state and the lowest vibrational state of the excited state), the HOMO and LUMO energy levels closely related to the electrochemical oxidation and reduction potentials of the dyes.
Figure 2.2: Molecular structures and formula weights of sensitizing dyes employed in this thesis work. Z907 (Paper IV), K77 (Paper II), D35 (Paper I), M3 (Paper I) and LEG4 (Paper III).
Table 2.1: Absorption and electrochemical properties of the dyes used in this thesis work.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E_{\text{HOMO}}$ V vs. NHE</th>
<th>$E_{0-0}$ eV</th>
<th>$E_{\text{LUMO}}$ V vs. NHE</th>
<th>$\epsilon$ M$^{-1}$ cm$^{-1}$</th>
<th>Abs$^{\text{max}}_{\text{nm}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z907</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12200</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>K77</td>
<td>0.97</td>
<td>1.75</td>
<td>-0.78</td>
<td>19400</td>
<td>546</td>
<td>84</td>
</tr>
<tr>
<td>D35</td>
<td>1.04</td>
<td>2.41</td>
<td>-1.37</td>
<td>30100</td>
<td>445</td>
<td>85</td>
</tr>
<tr>
<td>M3</td>
<td>1.07</td>
<td>2.30</td>
<td>-1.23</td>
<td>49000</td>
<td>485</td>
<td>86</td>
</tr>
<tr>
<td>LEG4</td>
<td>0.88</td>
<td>2.04</td>
<td>-1.16</td>
<td>49000</td>
<td>541</td>
<td>82</td>
</tr>
</tbody>
</table>

The $E_{0-0}$ transition energies of the dyes are estimated from the intercept of the normalized absorption and emission spectra. The LUMO energy levels of the dyes are estimated from the relation $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$ vs. NHE.

Usually the design and modification of molecular structure are employed as the tools in order to tune the energy levels of the electronic states of organic dyes. The most successful protocol for designing the organic dyes is based on a D-π-A molecular structure, which consists of an electron-rich donor group (D), a conjugated linker group (π) and an electron-deficient acceptor group (A), which lies close to or also functions as the anchor group binding onto the photoanode surface (Figure 2.3). The advantage of such a “push-pull” design is that the electron density of the HOMO is mainly located on the donor part of the dye molecule while the most density of the LUMO is located on the acceptor compartment. Therefore the intramolecular charge transfer occurs from HOMO to LUMO, i.e. from donor to acceptor, when the molecule is excited by photons. Such an intramolecular charge transfer facilitates the electron injection since the electron density is already located close to or on the anchor part of the dye molecule before injection. Consequently, the holes remain on the donor part of the dye molecules, which is relatively far away from the photoanode surface but close to the HTM molecules after injection. Therefore such a D-π-A molecular structure of dyes is beneficial for not only suppressing the charge recombination but also facilitating dye regeneration.

The donor group of organic dyes usually features a strong electron-rich core structure with large conjugated delocalized π bond (π molecular orbital), such as phenoxazine, indolines, alylamines. One family of the most successful core structures of donor group in organic dyes are the triarylamine derivatives in virtue of their excellent electron-donating properties, which are used in dye D35, M3 and LEG4 exhibiting high extinction coefficient compared to the conventional Ru-complex Z907. Featuring high electron conductivity offered by large aromatic systems, the linker group of organic dyes normally functions as an electron-transfer bridge to not only physically but also electronically connect the donor and acceptor parts based on the efficient π orbital electronic coupling with both terminals, therefore the elec-
tron density can be favourably transferred from donor to acceptor through the linker group with the electronegativity as driving force upon photoexcitation. The commonly used linker group can be constructed by the electron-rich thiophene unit due to its high electron conductivity, such as single thiophene (the linkers in D35 and M3) and multi-thiophene in connection as an aromatic system (the linker in LEG4). The acceptor group is usually comprised of a strong electron-withdrawing structure, which for simplicity sometimes also include the anchor group, such as cyanoacrylic acid, one of the most commonly used acceptor groups using carboxylic group to bind the dye molecules onto the TiO$_2$ surface by forming the chelating bond with the hydroxyl group of the TiO$_2$ surface.$^{87}$

Figure 2.3: Schematic molecular structure design of a D-$\pi$-A organic sensitizer, which is illustrated by the dye LEG4 with three compartments in such a D-$\pi$-A molecular structure.

The electronic properties of organic dyes can be readily tuned by modifying the three fragments. For instance, the absorption spectra of dye molecules can be red-shifted for harvesting more photons by the addition of a better electron conducting linker or stronger electron-withdrawing acceptor group. For instance, Figure 2.4 shows that the LEG4 sensitized TiO$_2$ electrode absorbs in a broader spectral region with a red-shift compared to that of D35 due to the effect that the multi-thiophene linker of LEG4 results in a larger conjugated system with more delocalized charge density than that of the smaller aromatic linker (single thiophene) of D35. Introducing long alkyl chains into the donor or linker group of the dye molecules was found to be a crucial modification of organic dyes since the long side chains tend to prevent dye aggregations by serving as spacers to separate the dye molecules bound on the TiO$_2$ surface and to prohibit the charge recombination by protecting the TiO$_2$ surface from the HTMs and the sites of the dye molecules with high hole concentrations.$^{88}$
It is worth noticing that the structure of D-π-A dye induces a molecular dipole moment along the dye molecule pointing from the partially negatively charged acceptor to the partially positively charged donor. When the dye molecule is anchored onto the TiO$_2$ surface, the molecular dipole moment often slightly shifts the conduction band edge of TiO$_2$ upwards, which consequently results in a beneficial $V_{oc}$ increase in the sDSC devices. Therefore the structure modification of dye molecules leading to the increase of molecular dipole moment can be used as a tool to improve the $V_{oc}$ of sDSC devices.

2.1.3 The hole transport materials

The electron injection from the dye into the conduction band of TiO$_2$ at the charge separation leaves the dye molecules in their oxidized form. Therefore, a hole transport material needs to be located between the dye molecules and the counter-electrode for regenerating the oxidized dye and transporting the holes out of the sDSC system. The hole transport is fulfilled by electronic conduction since the concept of hole arises from the description of an electron vacancy in the system. According to the energy diagram, in order to provide enough regeneration driving force, the HTMs ought to have a HOMO level more negative than that of the dye favoring the hole injection from oxidized dye into the HTM layer. In addition a good HTM ought to conduct holes in the fast manner with high hole-mobility, which significantly lowers the probability of charge recombination between the free electrons and the holes located in the HTM layer. The inter-molecular conjugation, typically
the π-π orbital coupling, becomes one of the dominating factors for hole conduction through HTM layer.

Since the dye molecules are attached usually in a monolayer on the surface of TiO₂ particles in the mesoporous electrode, such a dye monolayer needs to be fully covered by a thin layer of HTM following the curvature of the TiO₂ surface so that each dye molecule is in contact with HTM molecule in vicinity for efficient regeneration. Therefore the HTM needs to infiltrate through the mesoporous electrode as completely as possible during the device fabrication. So far, the most commonly used methods of applying the HTM into the sDSC devices are still based on the solution processing. Therefore the pore-filling is limited by the solubility of the HTM molecules in the organic solvents. In addition the manner how the HTM molecules stack with each other inside the pores during the formation of the HTM film accompanied by the solvent evaporating away determines the alignment, orientation and crystalline domain size of the HTM molecules in the formed film. The characteristic of the solvents used in the preparation step therefore directly influences the hole conduction property of the formed HTM layer. So far chlorobenzene was found to be the best solvent for dissolving organic HTMs in terms of HTM film formation. After the solution-processed preparation of HTM layer, for instance by spin-coating, there is an overstanding layer of the residual HTM remaining above the mesoporous electrode, the thickness of which can be readily tuned by changing the spin-coating parameters. The presence of this layer is essentially necessary to avoid direct contact between the counter-electrode (normally a deposited metal layer in sDSCs) and the TiO₂ surface in order to eventually protect the device from being shunted.

There are different types of HTMs developed for sDSCs, among which spiro-OMeTAD so far is proven to be the best HTM used for devices providing the record efficiencies. The comparison with other HTMs and the limitations of device improvement by using spiro-OMeTAD will be further discussed in the Chapter 3.

2.1.4 The interfacial functional additives

Additives are usually employed for interfacial modifications in sDSCs to further improve the device performance. The most two commonly used additives are shown in Figure 2.5, 4-tert-butylpyridine (t-BP) and lithium bistri-fluoromethylsulfonyl imide (Li-TFSI). These additives are usually introduced into the device in the preparation step of HTM layer by blending the additive materials into the HTM solutions, which therefore also play an important role on the formation of HTM layer inside the porous electrode.

In spite of the high volatility, the high boiling point of 196 °C allows t-BP to partially remain in the sDSC devices after the fabrication processes. The higher electronegativity of the pyridine ring and the electron-donating property of methyl group collectively result in an uneven charge density distribution along the molecule. The electron density on the aromatic ring in the
vicinity of nitrogen atom is relatively higher than that on the methyl terminal, which means a molecular dipole moment occurs pointing from the nitrogen to the methyl group. When infiltrating through the mesoporous electrode in the HTM solution, the lone pair of electrons on the nitrogen atom tends to coordinate onto the TiO$_2$ surface uncovered by dye molecules resulting in the adsorption of $t$-BP molecules at TiO$_2$ surface. As shown in Figure 2.6 similarly to the dipole moment of dye molecules at the interface, the manner of alignment that the dipole moment of $t$-BP molecule points away from the interface eventually leads to a favorable upward shift of the conduction band of TiO$_2$ that increases the $V_{oc}$ of the device slightly. $^{89}$ Moreover the formation of the interfacial $t$-BP layer restricts the charge recombination by separating the TiO$_2$ surface from the donor part of the oxidized dye and the HTM layer. $^{90,91}$

![Molecular structures of Li-TFSI and t-BP](image)

Figure 2.5: Molecular structures of two most commonly used additives in sDSCs, lithium bistrifluoromethylsulfonyl imide (Li-TFSI) and 4-tert-butylpyridine ($t$-BP).

The function of Li-TFSI at the interface is more complicated than that of $t$-BP although there is certain similarity. The Li-TFSI dissolves as a pair of counter-ions in HTM solution during process. The built-in potential across the device under illumination drives the Li$^+$ cations to diffuse towards the negatively charged TiO$_2$ surface. Consequently the Li$^+$ cations adsorb onto the TiO$_2$ surface to form a cationic monolayer compensating the free charges in the conduction band of TiO$_2$ while the TFSI$^-$ anion remains in the vicinity of donor part of the dye molecule to stabilize the oxidized dye as counter charge. Therefore the Li$^+$ cations function as a spacer between the injected electrons and the carriers of holes to screen the colomic interaction between charge carriers, which significantly inhibits the recombination at interfaces. $^{91-94}$ Paper III discusses the significance of Li$^+$ cations as surface modifier on TiO$_2$ and how the migration of Li$^+$ ions towards the photoanode surface dramatically influences the photovoltaic performance of sDSC devices, which shows that the devices essentially need the surface modification by Li$^+$ ions to function.

It is also observed that Li-TFSI causes a downward shift of the conduction band of TiO$_2$ resulting in an unfavorable $V_{oc}$ decrease in the DSC devices (Figure 2.6). $^{95}$ Moreover, it is suggested that the Li-TFSI improves the hole conductivity of the organic HTMs by creating a new pathway for hole
transport through the HTM layer, particularly in spiro-OMeTAD based sDSCs.\textsuperscript{96,97} It is observed that spiro-OMeTAD dissolved in organic solvent, such as chloro-benzene, hardly get oxidized when stored under light while the oxidation takes place slowly in the presence of Li-TFSI.\textsuperscript{98} Such an effect has been studied and interpreted by proposed mechanism that Li-TFSI is required as a catalyst involved in the oxygen-induced photo-doping of spiro-OMeTAD, which increases the initial concentration of oxidized spiro-OMeTAD, i.e. the charge density of holes in the HTM layer facilitating the hole conduction.\textsuperscript{99}

**Figure 2.6**: Illustration of energy level shifts of conduction band of TiO\textsubscript{2} depending on the presence of functional additives at the interface, where t-BP shifts \(E_{\text{CB}}\) of TiO\textsubscript{2} upwards for a \(V_{\text{oc}}\) increase while Li-TFSI shifts it downwards for a \(V_{\text{oc}}\) decay.

Apart from t-BP and Li-TFSI there are many other additives that can be used in sDSC device. For instance, the deoxycholic acid is normally used in the dye-sensitization bath as a spacer between dye molecules on TiO\textsubscript{2} surface to prohibit dye aggregation so that the photocurrent can be improved. In general the functions of employing these additives remain the same aiming for improving the photovoltaic performance of the devices by suppressing the charge carrier recombination and enhancing the output photo-current and voltage.

### 2.1.5 The counter-electrode

On top of the residual layer of HTMs a counter-electrode is required as the back contact to complete the internal circuit and to function as an electrode providing current and voltage for the external electrical work. The materials of the counter-electrode ought to be photo-, thermal and electrochemical stable with high conductivity to provide an ohmic contact for minimizing the total series resistance across the sDSC devices. The most commonly used counter-electrode is evaporated metal layer by physical vapour deposition (PVD), such as Au and Ag. In most cases Ag is more favourable to serve as the counter-electrode since apart from its high conductivity the reflectance of
Ag is much higher than Au, which leads to an enhanced photon capture by reflecting the transmitted photons back into the dye-sensitized light harvesting layer. The enhanced light capture therefore improve the LHE and eventually contributes to the increased photocurrent. Particularly in the sDSC devices the thin layer of dye-sensitized TiO$_2$ electrode is one of the major limitations responsible for the losses in light harvesting and photocurrent. This approach therefore becomes the most facile way to achieve photon management to improve the energy conversion efficiency of these devices. The thickness of Ag counter-electrode is usually around 200 nm with sufficient reflectivity. On the other hand, the highly conducting carbon nanotubes (CNTs) are also developed as the counter-electrode for sDSCs due to its low cost and solution-processability. However, the aim of developing the counter-electrode materials remains the same, i.e. in order to provide a cost-effective back contact with minimized contribution to the total series resistance across the sDSC devices.

2.1.6 The interface reactions in sDSC

The operating mechanism of sDSCs can be described by several interfacial electron transfer reactions in cooperation. Each reaction can be kinetically described by its reaction rate constant. Figure 2.7 illustrates all electron transfer reactions occurring at the interfaces in sDSC. For simplicity these reactions can be divided into two groups: the desirable forward reactions including photo-excitation, electron injection, dye regeneration, electron transport in TiO$_2$ and hole conduction through HTM; the unfavorable backward reactions, such as the relaxation of photo-excited state of the dye, the recombination between free electrons and oxidized dye molecules and the recombination between free electrons in TiO$_2$ and holes in HTM layer. Among these interfacial ET reactions, the forward reactions benefit the charge separation and therefore contribute to the energy conversion while the backward reactions represent the charge recombination reactions and therefore become the limitations of photovoltaic performance in sDSC devices. Hence the three backward ET reactions account for the mechanism of the major losses in the electrical power output of the sDSCs.

The competition in terms of kinetic reaction rate constants between the forward and backward ET reactions collectively determines whether and how efficiently the solar cell device can covert the solar irradiance into electrical power. The greater net difference between these two groups of rate constants is obtained in the device, the more efficient charge separation and collection would be gained and therefore the higher overall energy conversion efficiency of the solar cell devices would be eventually achieved.
Figure 2.7: Schematic illustration of the interfacial electron transfer reactions in sDSCs. Forward reactions contributing to the energy conversion are marked in green solid lines while backward reactions limiting the photovoltaic performance are marked in red dotted lines.

Upon photo-excitation, the dye molecule absorbs a photon to form its excited state with higher energy level compared to that of TiO$_2$ conduction band (reaction 1). Within the lifetime of excited state the dye molecule either injects an electron into the conduction band of TiO$_2$ through the anchor group (reaction 2), or relaxes back to the ground state by irradiative or non-irradiative decays (reaction 6).

\[
\begin{align*}
D + h\nu & \rightarrow D^* & 1. \text{ Photo-excitation} \\
D^* & \rightarrow D^+ + e^- & 2. \text{ Electron injection} \\
D^* & \rightarrow D (+h\nu) & 6. \text{ Dye relaxation}
\end{align*}
\]

The reaction kinetics suggests that the electron injection from the photo-excited state of dye into the TiO$_2$ conduction band takes place in the range of femtosecond (fs, $10^{-15}$ s) to picosecond (ps, $10^{-12}$ s) while the lifetime of the photo-excited state lasts in nanosecond (ns, $10^{-9}$ s) range before relaxation. Therefore the interfacial ET reaction rate constant of electron injection ($k_{inj}$) is orders of magnitude greater than that of dye relaxation ($k_{rel}$), which lead to a favourable electron injection efficiency ($\phi_{inj}$) defined in Equation 2.5. Usually dyes have sufficiently long lifetimes for enough driving force of the electron injection. However, the influence of the interfacial additives needs to be taken into account as well. For instance, t-BP shifts the TiO$_2$ conduction band upwards leading to an increased $V_{oc}$ but meanwhile it lowers the electron injection driving force.
After electron injection, the dye remains in its oxidized form, which is further regenerated by the electrons from HTM (reaction 3). On the other hand, the charge carriers recombination of the free electrons in the TiO₂ acceptor (mainly the conduction band) to the oxidized dye molecules (reaction 7) or to the holes located on HTM (reaction 8) competes with dye reduction.

\[
\begin{align*}
&\text{D}^+ + \text{HTM} \rightarrow \text{D} + \text{HTM}^+ &\quad \text{3. Dye regeneration} \\
&\text{D}^+ + e^- \rightarrow \text{D} &\quad \text{7. Recombination with hole on D}^+ \\
&\text{HTM}^+ + e^- \rightarrow \text{HTM} &\quad \text{8. Recombination with hole on HTM}
\end{align*}
\]

It is reported that the dye regeneration by solid-state HTMs in sDSCs takes place in the range from ps to ns competing with the recombination of electrons to the oxidized dye molecules or to the holes carried by HTM layer in the range of microsecond (\(\mu\text{s}, 10^{-6}\text{s}\)) to millisecond (ms, \(10^{-3}\text{s}\)). In general, the rate constant of dye regeneration \((k_{\text{reg}})\) needs to be greater than that of recombination to hole carrier species \((k_{\text{rec}})\) in order to yield a high regeneration efficiency \((\varphi_{\text{reg}})\), which is defined in similar manner to \(\varphi_{\text{inj}}\) determined by the following equation:

\[
\varphi_{\text{reg}} = \frac{k_{\text{reg}}}{k_{\text{reg}} + k_{\text{rec}}} 
\]

Since the regeneration of oxidized dye molecules is normally three orders of magnitude faster than the charge recombination (reaction 7), the regeneration efficiency of sDSCs is therefore usually assumed to be approximately unity. For instance, the rate of hole injection from a ruthenium dye, typically N719, to spiro-OMeTAD was experimentally determined to be in the range between ps to ns with more than half portion of the oxidized dye being reduced within 900 ps. However, the insufficient pore filling of HTMs due to their large molecular structure and low solubility might lead to the incomplete regeneration of oxidized sensitizers and therefore lower \(\varphi_{\text{reg}}\).

Unlike the charge transport in the conventional \(p-n\) junctions, the injected photo-induced electrons are transported through the mesoporous TiO₂ electrode by diffusion-controlled process rather than drift current. However the two pathways of recombination of free electrons to either the oxidized dye molecules or the hole carrier of HTMs compete with the electron transport. The kinetic rate constant of the electron diffusion through TiO₂ \((k_{\text{trans}})\) must be greater than that of the recombination \((k_{\text{rec}})\) in order to successfully collect the separated charge carriers with a favourable charge collection efficiency \((\varphi_{\text{cc}}\text{ defined in Equation 2.7})\) to provide the electrical power in external circuit.
Generally speaking in the conventional solar cells based on the p-n junctions, the equilibrium aligning the quasi-Fermi levels in the p- and n-doped semiconductors results in the band-bending at the interface of the p-n junctions when the p- and n-doped semiconductors are placed in contact with one another. An internal electric field in the depletion region establishes as the driving force to separate and transport the charge carriers into the bulk materials by drift current. The photo-excitation causes the redistribution of charge carrier concentrations leading to the shifts of quasi-Fermi levels in p-n junctions.

However, the mesoporous TiO$_2$ electrode is comprised by a number of inter-connected nanoparticles with relatively small diameters, normally in the scale around 20 nm, which in general are n-doped with a low doping density around $10^{17}$ cm$^-3$. Unlike the conventional p-n junctions, it is therefore observed that the band-bending is neglected in such a network composed by nanoparticles surrounded by ions in the electrolyte with the absence of internal electric field. Instead, a concentration gradient of the injected electrons in the TiO$_2$ electrode appears to be the major driving force for the electron transport by diffusion through the mesoporous network towards the FTO substrate. The diffusion-controlled electron transport can be described by a trapping-detrapping mechanism depending on the density of the trap states in the band gap of semiconducting TiO$_2$ electrode.

![Figure 2.8: Schematic diagram of the electron transport in the mesoporous TiO$_2$ electrode by diffusion with concentration gradient as driving force. The electron transport is described by the trapping-detrapping mechanism that the injected free electrons might be trapped in the band gap states of the semiconductor and the electron transport continues when the trapped electrons are thermally detrapped back into the conduction band of the semiconductor electrode.](image-url)
As illustrated in Figure 2.8, there are certain localized energy states between the conduction band and the valence band (VB) of the TiO$_2$ semiconductor, which are termed as band gap states. The photo-induced injection of free electrons into the conduction band of TiO$_2$ is followed by the electron transport process. Due to the extraction of electrons from the FTO substrate side at working conditions, the gradient distribution of electron concentration declines along the mesoporous TiO$_2$ to its lowest value in the FTO. By the absence of internal electric field, such a relatively small driving force leads the free electrons to travel along certain distance before they are trapped in the band gap states. The trapped electrons can be thermally detrapped back into the diffusion transporting towards the FTO substrate. The photocurrent is detected in the external circuit once the free electrons are collected at the conducting electrode after they encounter through a series of trapping-detrapping processes.

The chemical diffusion coefficient ($D_n$) is commonly used to characterize the electron diffusion process, which is defined in Equation 2.8, where the $n_t$ denotes the concentration of trapped electrons while the $n_c$ and $D_0$ designate the concentration and the diffusion coefficient of the free electrons in TiO$_2$ conduction band respectively.

$$D_n = \left(1 + \frac{\partial n_t}{\partial n_c}\right)^{-1} D_0 \quad (2.8)$$

Therefore the $D_n$ can be regarded as an effective electron diffusion coefficient, which is light intensity dependent due to the contribution from the dynamic equilibrium between the trapped electrons in band gap states and the free electrons in TiO$_2$ conduction band.

According to Equation 2.8, higher concentration of free electrons in TiO$_2$ conduction band advances the diffusion of electron transport since $D_n$ approaches its maximum in the vicinity of $D_0$ meanwhile the probability of electron recombination to hole carrying species however unfavourably becomes higher as well. Thus, a compromise needs to be considered between the faster electron diffusion and the longer electron lifetime ($\tau_n$), the latter is described in Equation 2.9 characterizing how fast the recombination processes occur.

$$\tau_n = \left(1 + \frac{\partial n_t}{\partial n_c}\right) \tau_0 \quad (2.9)$$

Where the effective electron lifetime becomes shorter and shorter approaching its minimum in the vicinity of the constant free electron lifetime ($\tau_0$) when the equilibrium distribution of conduction band electrons over trapped electrons ($\frac{\partial n_c}{\partial n_t}$) becomes greater and greater resulting in a higher probability
of recombination with greater $k_{\text{rec}}$. In order to characterize the balance between electron diffusion coefficient and lifetime by quasi-static approximation, the electron diffusion length ($L_D$, defined in Equation 2.10) is commonly used to describe how far an electron can diffuse through the mesoporous electrode before recombination occurs on average.\footnote{106}

$$L_D = \sqrt{D_n \tau_n} \tag{2.10}$$

The $L_D$ no longer depends on light intensity since the inverse effects on $D_n$ and $\tau_n$ cancel out with each other. Since $L_D$ represents the average displacement of the diffusing transport of an injected electron through the TiO$_2$ electrode in general an electron diffusion length exceeding the TiO$_2$ film thickness is required in order to obtain the high charge collection efficiency in sDSC devices.

The regeneration of the oxidized dye is accomplished by hole injection into the HOMO level of the HTM molecules followed by hole transport through HTM layer towards the counter-electrode. Unlike the liquid electrolyte DSCs, it is suggested that instead of the charge transport by ionic diffusion of the charge carrier redox couple, the hole transport in sDSCs is based on an electronic hopping mechanism through a disordered spatial and energetic HOMO substates subject to a Gaussian distribution.\footnote{102,110-112} In general the charge transport is performed by the charge carrier transporting materials in three different manners including the transport of the negative charge carrier (electron), the transport of the positive charge carrier (hole) and the transport of both charge carriers simultaneously (ambipolar charge transport). The conductivity ($\sigma$) of the ambipolar charge transporting materials is used to characterize how fast the electric current can be conducted through the conducting material, as specified in Equation 2.11 which can be described as a function of the mobilities ($\mu$) and the concentrations ($c$) of the two charge carriers in these materials, where the $\mu$ characterizes how fast the charge carrier can be transported through a conducting material, the $e$ is the elementary charge, the $n$ designates electrons while the $p$ denotes holes.

$$\sigma = e\mu_n c_n + e\mu_p c_p \tag{2.11}$$

The commonly used organic HTMs, such as spiro-OMeTAD, tend to form a solid-state amorphous glassy phase rather than regular crystalline phases when they are applied from solution by infiltration into the mesoporous electrode.\footnote{113,114} The disordered structure of such a phase in terms of the molecular orientations therefore becomes a crucial factor influencing the charge carrier transport through the HTM layer. It is observed that the concentration of negative charge carrier is negligible in most organic HTMs when they function as the hole transporters in sDSC devices. Thus the conductivity of charge transport in this case becomes independent on the electron mobility...
(μ_n) according to Equation 2.11, the hole-mobility (μ_p) and the hole concentration (c_p) in these HTMs therefore have been investigated as the primary parameters determining the hole transporting performance of the HTM layer in sDSC devices. As previously reported, hole-mobility of spiro-OMeTAD in its pristine form was measured as the following values: 1.0 × 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}, 1.4 × 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}, 4.0 × 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}, 2.0 × 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}, which vary by one order of magnitude in units due to the different experimental methods adopted, namely the time-of-flight mobility measurement and the space charge limited current (SCLC) measurement. In fact, such a relatively low hole-mobility of spiro-OMeTAD becomes the limitation of the device performance in sDSCs. Therefore, according to Equation 2.11 the approaches increasing the initial hole concentration in spiro-OMeTAD by addition of p-type dopants have been developed as the important alternative way to improve the hole conduction in the sDSC devices using organic HTMs with moderate hole-mobilities.\textsuperscript{96,97}

2.1.7 The limitations on photovoltaic performance in sDSC
As discussed above, fast charge recombination in sDSC lead to low charge collection efficiencies and eventually low power conversion efficiencies. The electron diffusion length at working conditions in the vicinity of open-circuit was determined to be no more than the optimal film thickness approximately around 2 μm in sDSC devices, which contributes to the increases probability of charge recombination.\textsuperscript{116,117} While at working conditions close to short-circuit the electron diffusion length is measured to be long enough to achieve decent charge collection efficiencies.\textsuperscript{118,119} Therefore approaches improving the charge transport through the TiO\textsubscript{2} layer ought to be one way to prolong the electron diffusion length to inhibit recombination for better device performance, such as employing more structurally ordered TiO\textsubscript{2} or enhancing the conductivity of the TiO\textsubscript{2} by dopants. The optimal film thickness of the light harvesting layer is limited to be around 2 μm in sDSC devices, which is considerably thin compared to liquid electrolyte based DSCs. Such a thin active layer results in a low photon harvesting efficiency due to the insufficient light absorption, especially in the red and near-IR spectral regions, which can be normally characterized in terms of the photocurrent loss in the incident photon to current conversion efficiency (IPCE) spectrum. As mentioned in section 2.1.2 one of the mostly used strategies to compensate such a photocurrent loss is to employ dye molecules with high extinction coefficients and broadened absorption spectra.\textsuperscript{120,121} In particular organic dyes have been developed according to the principles in order to increase the light harvesting and protecting the TiO\textsubscript{2} surface to prohibit the charge recombination at the dye/TiO\textsubscript{2} interface.\textsuperscript{122}

The optimized film thickness in sDSC devices is constrained to be thin not only due to the short electron diffusion length but also due to the insufficient pore filling of HTMs through the mesoporous electrode.\textsuperscript{54} The inefficient
infiltration of HTMs into the TiO$_2$ network is usually caused by the limitations of the techniques used to form the HTM layer in the device structures. In this case, the dye molecules might not be completely in contact with HTM molecules, therefore the dye regeneration processes might not efficiently proceed, which significantly harms the device performance. Thus, in this thesis work, in terms of method and materials development the schemes how to improve the pore filling of HTMs into the mesoporous film is investigated as one of the most important aspects limiting the device performance.

Apart from those discussed above, the relatively low hole-mobility of the most commonly used organic HTMs increases the probability of charge recombination, which decreases the charge collection efficiency as well. In this thesis, the investigation is therefore focused on how different HTMs and the different methods to form the HTM layer influence the photovoltaic performance of the sDSC devices. On the other hand, the stability of sDSCs still remains less studied compared to the discussions focused on the materials development, structure modification and understanding the working principles. However, in terms of commercialization and large-scale production the research into reliability of sDSC devices become a more and more important issue.

2.2 Organometallic halide perovskite based solar cells

Based on the knowledge acquired over more than twenty years during the development of DSCs and OPVs, the organometallic halide perovskite based solar cells offer a new approach of light to current conversion photovoltaic devices, which have attracted a number of interest due to its considerably high power conversion efficiencies. This type of devices feature low fabrication cost, strong light harvesting properties and low rates of the non-radiative charge carrier recombination, which still remain as the limiting factors in sDSC devices.

2.2.1 The organometallic halide perovskite light absorbers

Similar to sDSCs, the organometallic halide perovskite based solar cells also comprise the light absorber layer and hole transport material layer collectively fulfilling the charge separation through the organic/inorganic heterojunction device with analogous structures. The main difference between these two types of MSCs lies in the light harvesting materials and the transport of the negative charge carrier. Unlike the sDSCs, perovskite based solar cells capture light by the organometallic halide perovskite instead of dye molecules. Perovskite was named after the Russian mineralogist Perovski referred to the crystal structure commonly described by the formula of ABX$_3$, where the B normally denotes a transition metal cation, the X designates an anion.
(usually halides are employed) and the A stands for an organic cation, usually alkylammonium ions with tunability in terms of different sizes.

Figure 2.9: Schematic crystal structure of perovskite absorber. where the A and B stands for cations while the X denotes anion. In the high-efficiency perovskite based MSCs, the A is usually the methylammonium ion (CH$_3$NH$_3^+$), the B is the relatively smaller Pb cation and the X normally is the halogen ion I$^-$ (of particular interest, Cl$^-$ and Br$^-$ could also be used in the formula).

The crystal structure of perovskite light absorber is described in Figure 2.9 in association with an octahedral factor $\mu$ and a tolerance factor $t$, where $\mu$ is defined as the ratio of $R_B$ over $R_X$ and $t$ is defined in Equation 2.12 characterizing the ratio between the bond length of A-X over the bond length of B-X in the ideal model of solid sphere, where $R_A$, $R_B$ and $R_X$ denote the ionic radii of the corresponding ions.$^{123}$

$$t = \frac{R_A + R_B}{\sqrt{2} (R_B + R_X)} \quad (2.12)$$

In the crystal structures of perovskite absorbers using halides as X anions, in general $t$ is determined between 0.81 and 1.11 while $\mu$ is measured from 0.44 to 0.90. Usually the less orthorhombic or symmetric tetragonal structures would be obtained when the value of $t$ becomes lower and lower, therefore the cubic structure shown in Figure 2.9 tends to appear when $t$ occurs in the narrow window of 0.89-1.0. However, the cubic crystal structures of the given perovskite absorbing materials are likely obtained by well-controlled heating processes due to the favourable high-temperature phase transitions between these crystal structures.$^{124}$ So far, for high-efficiency perovskite based MSCs, the commonly used component B is either Pb with $R_B$ of 0.119 nm or Sn with $R_B$ of 0.110 nm, which forms the perovskite compounds featuring low bandgaps with enhanced photon absorption in the red and near-IR
spectral regions. However, it has been proven that Pb remains the dominant material in terms of record efficiencies and device reliabilities due to the fact that Sn based perovskite compounds tend to be readily oxidized in the presence of iodide harming the device stability. The anion X is usually a halogen, such as I\(^{-}\), Cl\(^{-}\) and Br\(^{-}\), in particular cases even F\(^{-}\) could be considered. In spite of the diversity of halide anions, in order to obtain high-efficiency devices mixed halide precursors are normally applied in the formation of the perovskite layer. The most commonly used cation A appears the largest in size, which usually comprises organic alkylammonium groups, such as methylammonium (CH\(_3\)NH\(_3\))\(^{+}\) and ethylammonium (CH\(_3\)CH\(_2\)NH\(_3\))\(^{+}\), in particular cases formamidinium (NH\(_2\)CH=NH\(_3\))\(^{+}\) also provides perovskite compounds with competitive photovoltaic performance. At present, the typical perovskite compound with the formula of CH\(_3\)NH\(_3\)PbI\(_3\) or CH\(_3\)NH\(_3\)PbI\(_3-x\)Cl\(_x\) derived from the different preparation methods provides the best MSC devices in terms of power conversion efficiencies and stabilities.

In general, perovskite based MSCs provide remarkably high photocurrent in comparison with sDSCs. Such a high current output is mainly attributed to the high absorption coefficients of the perovskite absorbers. The absorption coefficient of lead halide perovskite is measured to be one order of magnitude higher than that of the best organic dye molecules. In addition the absorption spectrum of lead halide perovskite appears to be considerably broadened, which covers the entire visible region and partially the near-IR range of the solar spectrum, generally with a prolonged absorption tail stretching even beyond 850 nm leading to a high LHE.\(^{68,71}\)

One of the facile advantages of using perovskite materials as light absorber is that their photoelectronic properties can be readily tuned by modifying the compositions. Various combinations and mixed compounds of A, B and X can be investigated to tune the photoelectronic properties, such as absorption spectra, bandgaps and the energy levels of CB and VB edges. As shown in Figure 2.10, it can be clearly concluded that the bandgap of perovskite compounds is enlarged by extending the length of the alkyl chain that increases the size of the organic cation A. The extension from methyl to ethyl group in the organic cation A slightly enlarges the cation size, which therefore introduces a small distortion character in the perovskite geometry leading to a somewhat deviation from the ideal cubic crystal lattice that further induces the broadening of the perovskite bandgap and absorption spectra. For instance, the bandgap of CH\(_3\)CH\(_2\)NH\(_3\)PbI\(_3\) with 2.2 eV is reduced to 1.5 eV for CH\(_3\)NH\(_3\)PbI\(_3\) due to the shortening of alkyl group in cation A.\(^{131}\) Similarly by adjusting the ratio between different halides in the formula the properties of perovskite compounds can also be modified. Such a tunability enables facile optimization of perovskite as light absorbing layer especially in terms of broadening the absorption spectra in order to harvest more photons for higher LHE.
2.2.2 The operating mechanisms and limitations in perovskite based sMSCs

In the perovskite based MSCs using mesoporous TiO$_2$ as photoanode, the operating mechanism is similar to that of sDSCs (Figure 2.11, left). The absorption of incident light by the perovskite layer induces the photo-excitation transitions between the electronic states of perovskite. Subsequently the difference in energy levels between CB edges of TiO$_2$ and perovskite generally provides sufficient driving force to facilitate the photoelectron injection into the CB of TiO$_2$ followed by the electron transport through the mesoporous electrode according to a trapping-detrapping dynamics. However, there is an argument stating that the electron transport through the perovskite layer might also partially contributes to the total charge carrier transport due to the recently observed fact that the $V_{oc}$ of perovskite based MSCs mainly depends on the energy difference between the HOMO level of HTMs and the electron quasi-Fermi level in perovskite rather than that in TiO$_2$ photoanode. This might be the reasonable explanation why perovskite based MSCs normally exhibit much higher $V_{oc}$ than sDSC devices. Such an observation also indicates that apart from absorbing photons the exciton diffusion, charge separation and charge diffusion can also be accomplished through the perovskite layer due to the sufficiently long electron-hole diffusion length.

Therefore, as shown in Figure 2.11 (right), the perovskite based MSCs with structures beyond sensitized model have been developed by replacing the semiconducting TiO$_2$ photoanode with the wider bandgap metal oxide Al$_2$O$_3$. In this case, the electron injection is prohibited since the bandgap of...
Al₂O₃ is too large for electron injection from the perovskite to the Al₂O₃, which acts as nothing more than an insulating mesoporous scaffold only providing a large surface area to carry perovskite for higher LHE. Thus, this type of MSC devices operate in a slight different way since no electron injection occurs after photo-excitation due to the effect that the conduction band of Al₂O₃ appears at a higher energy level with regard to that of the excited state of perovskite, apart from the light absorption the electron conduction is therefore also accomplished through the perovskite layer itself due to the sufficient charge diffusion length.

Figure 2.11: Schematic operating mechanism of perovskite based MSCs, where the electron injection into the TiO₂ CB is followed by the electron transport through the mesoporous TiO₂ layer according to the trapping-detrapping dynamic theory in the presence of TiO₂ scaffold while the electron transport is carried on through the perovskite layer in the presence of Al₂O₃ scaffold without electron injection occurring.

Hence, the charge diffusion length becomes one of the most significant limiting factor for the photovoltaic performance of perovskite based MSCs. Particularly the film thickness is directly limited by such an effect, i.e. the optimal active layer thickness in these devices usually appears around 400 nm without exceeding the average charge diffusion length. Such an effect can be more clearly observed in planar structure designs of thin film heterojunction MSCs using perovskite as light absorber. The optimized film thickness is further reduced down to 330 nm in thin film perovskite based MSCs with perovskite layer prepared by vapour deposition.

On the other hand, limitations can be found during the preparation processes of the HTM layer as well. The hole transport materials used in perovskite based MSCs have been adapted from those developed for sDSCs with spiro-OMeTAD still being the most utilized one. Moreover, solution-based process, such as spin-coating, still remains the most commonly used method to apply the HTM layer in perovskite based MSCs, which also leads to the
waste of materials and the difficulties for scaling up the device production. Therefore the needs to develop novel HTMs with higher hole-mobility and cheaper synthetic cost and to improve the preparation methods become more and more urgent.

To date, the perovskite based MSCs with highest efficiencies mainly utilize Pb as anion B causing the toxicity issue during device fabrications and disposal. This also introduces difficulties for the device encapsulation and protection from degradation since the leakage of lead during any manner of degradation could lead to severe environmental issues. Moreover, these MSC devices generally undergo rapid degradations on exposure to moisture and ultraviolet radiation. Therefore the paradox that Pb is toxic and environmental-harmful but also necessary as the most important component for perovskite based MSC to function becomes one of the major drawbacks for this type of MSCs in terms of commercialization and up-scale production.

Despite of the shortages of perovskite based MSCs discussed above, the power conversion efficiency has been further improved up to 19.3% by Yang Yang et al. recently with modified interfacial geometry of device architectures, which highly inspires researchers to further develop such an emerging technology in terms of the developments of materials and device structures.
3. Hole transport materials

In the state-of-the-art architectures of solid-state mesoscopic solar cells, the separation of charge carriers often takes place at the interfaces facilitating the subsequent transports of charge carriers towards the respective electrodes for charge collection, where the hole transport materials play an important role to regenerate the oxidized states of the light absorbers and to conduct holes in a highly efficient manner meanwhile to prohibit the charge recombination on the pathway to the counter-electrode.

According to the operating mechanism of sMSCs, HTMs ought to have a more negative HOMO energy level than that of light absorbers in order to provide sufficient driving force in free energy for efficient regeneration of the oxidized species of the light absorbers. In addition, HTMs ought to have high hole-mobilities for fast hole conduction towards the counter-electrode, which meanwhile sufficiently suppresses the probability of charge recombination between the free electrons in the electron conducting material and the holes located in the HTM layer. Moreover, for the stability of the sMSC devices, HTMs ought to be physically and chemically stable on exposure to photons, electric fields and moisture. In terms of commercialization and up-scalable production of sMSCs, HTMs also ought to be cost-effective, recyclable and environmental-friendly. In this thesis work, the focus is aimed on the investigation and discussion of the different types of HTMs and the possible approaches to form the HTM layers and their influence on the photovoltaic performance in sMSC devices.

3.1 The solution-processible HTMs

During the fabrication processes of sMSC devices, the HTM layer is usually deposited by solution processing, such as spin-coating or screen-printing. Therefore most HTMs used in sMSCs are solution-processible in commonly used organic solvent, particularly in chlorobenzene, which generally dissolves HTMs with sufficiently high concentration to form a smooth thin layer at the interfaces. Since the hole transport through HTM layer in sMSCs depends on the electronic conduction rather than ionic mass transport the crystal domain size and the molecular stacking orientation of the formed HTM film become significantly crucial for the performance of hole conduction. Thus, apart from the intrinsic properties of the HTM compounds the
characteristics of the employed solvents appear essential in the processes of the formation of the HTM layer.

In general, the solution-processible HTMs can be classified into two major groups in terms of the chemical formula, namely the inorganic HTMs and organic HTMs. In the early stage of the development of sDSCs, an inorganic compound CuI was initially introduced into the system functioning as the HTM for hole conduction. The formation of CuI layer as a p-type semiconductor was further optimized by precipitation from MeCN solution, which in association with an organometallic sensitizer eventually exhibited a high power conversion efficiency of 3% in spite of the performance limitation arriving from the fast photo-degradation of the precipitated CuI layer under operating conditions. According to the similar synthetic scheme, inorganic material CuSCN was also utilized as a p-type hole conductor in sDSC devices, which performs as competitively as in liquid electrolyte based DSCs in terms of the electronic properties of the charge carrier transport. In addition, NiO and CuBr-based sulfide compounds have also been employed as HTMs resulting in measurable efficiencies. However, in general these inorganic HTMs suffer from low hole-mobilities leading to orders of magnitude faster recombination reactions of charge carriers compared to that in the conventional DSCs. Recently Kanatzidis et al. reported an inspiringly high efficiency of 8.5% by using an inorganic p-type direct bandgap semiconductor CsSnI$_3$ in combination with N719 sensitized TiO$_2$ mesoporous photoanode. The CsSnI$_3$ was observed as a distorted three-dimensional perovskite structure when it is applied as the HTM layer in mesoporous electrode. With considerably high hole-mobility of 585 cm$^2$V$^{-1}$s$^{-1}$ and suitable bandgap of 1.3 eV, the sDSC using CsSnI$_3$ as HTM eventually exhibits a surprisingly high photocurrent density of 19.2 mAcms$^{-2}$ that appears the highest record for sDSCs at the moment. However, in terms of long-term stability CsSnI$_3$ suffers from the oxidation-induced degradation in ambient environment.

Compared with inorganic HTMs, organic HTMs have been intensively studied due to their anticipated advantages, such as high solubility in commonly used organic solvents, suitable hole-mobility, thermal and photocatalystability and tunability of electronic properties. For simplicity, the solution-processible organic HTMs can be divided into two major categories in terms of molecular weight, namely the conjugated polymer HTMs, such as P3HT (Figure 1.6) and the small molecule organic HTMs, such as spiro-OMeTAD (Figure 1.6).

Inspired by the knowledge gained in OPV research field, conjugated polymers with remarkably high hole-mobility have been investigated as HTMs in sMSC. So far the device efficiencies still remain much lower than those using small molecule organic HTMs mainly due to the infiltration problem of the polymer molecules into the mesoporous electrode. In the architectures of sMSCs, mesoporous metal oxide photoanode comprised by annealed network of nanoparticles is commonly adopted in order to increase the sur-
face area for enhanced light absorption. When the most facile preparation method of solution-processible spin-coating is applied, the limited capability of dissolving polymer HTMs with large molecular weights in organic solvents becomes a significant limiting factor, which constrains the pore filling of polymer HTMs into the mesoporous electrodes. For instance, the most successful polymer HTM used in sMSCs, namely P3HT (Sigma-Aldrich, MW 15 000 - 45 000) can be dissolved in chlorobenzene with its highest concentration only reaching around 20 mg/mL. The comparison between P3HT and spiro-OMeTAD as different types of HTMs in terms of device performance will be further discussed in Chapter 5 (Paper I). Such an insufficient pore filling generally results in the inefficient regeneration of oxidized light absorbers and increases probability of charge recombination. To cope with such a problem, *in-situ* photoelectrochemical polymerization (PEP) has been employed in this thesis (Paper IV) to produce polymer HTM directly inside the mesoporous TiO$_2$ electrode, which will be discussed in details in the following section 3.2 in terms of operating mechanism and device performance.

On the other hand, the commonly used polymer HTMs in general exhibit strong absorption spectra partially covering the UV-visible spectral region due to the large conjugated chromophore groups in their molecular structures, which to some extent overlaps with the absorption spectra of the light absorbers and therefore might act as a filter layer competing the absorbers without contributing to the output photocurrent. Therefore the molecular design of HTMs without overlap in absorption spectra compared to that of light absorbers becomes a highly notable aspect in the application of sMSC devices.

Compared with large molecule polymer HTMs, small molecule organic HTMs have shown greater potential in sMSC systems in terms of weak light absorption, tunable electronic properties, high solubility in organic solvents and so forth. Based on the knowledge of HTM layer from the organic light emitting diode (OLED) research field, this type of HTMs are mainly designed and synthesized as small organic molecules, which usually exhibit relatively low absorption in the UV-visible spectral region.

Due to their high conductivity, the triarylamine based core structures have been realized to be one of the best choices as the basis for constructing high-performance organic HTMs. In particular, the electron-rich triphenylamine core with relative planar structure becomes the most popular starting point in the design and development of organic HTMs. Figure 3.1 exhibits some of the triphenylamine core based small molecule organic HTMs showing satisfactory performance in sMSC devices. Durrant *et al.* designed a series of triphenylamine-based organic hole conductors (HTM1-6, Figure 3.1) with varied molecular weights and mobilities and further investigated the influence of these HTMs on the hole-transfer yields at the dye/HTM interfaces by employing transient absorption spectroscopy.\textsuperscript{144} It was observed that the photocurrent output is directly proportional to the hole-transfer yield depend-
ing on the extent of pore penetration of HTMs in the mesoporous electrode. Such a mechanistic investigation on triphenylamine-based HTMs emphasizes the importance of efficient pore filling and interfacial energetics rather than hole conductivity in terms of device performance in sMSCs.

\[
\begin{align*}
\text{HTM1} & : \mu = 4.86 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{HTM2} & : \mu = 8.07 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{HTM3} & : \mu = 1.76 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{HTM4} & : n = 7, \mu = 2.06 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{HTM5} & : n = 15, \mu = 8.23 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{HTM6} & : n = 18, \mu = 1.04 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{TPAA} & : \mu = 3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{MeO-TPD} & : \mu = 8.23 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{AS37} & : \mu = 5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\text{AS44} & : \mu = 1 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}
\end{align*}
\]

Figure 3.1: Molecular structures of solution-processible small molecule organic HTMs used in sDSCs with the specified values of hole-mobility, including HTM1-6, TPAA, MeO-TPD, AS37 and AS44.

To date, the sMSC devices with best power conversion efficiencies still utilize spiro-OMeTAD as HTM, which belongs to a category of materials termed amorphous molecular glass. These materials are characterized by the disorder factor in terms of their intermolecular distance and stacking orientation in their solid-state glass phase, a phase at thermodynamical non-equilibrium. The thermal stability of the molecular glass state is usually
evaluated by the glass transition temperature ($T_g$), where the phase transition occurs from the fragile amorphous glass state to the moldable elastic phase. In order to improve the thermal stability, based on the maternal moiety of fluorene the spiro-carbon center was therefore initially introduced into the molecular structure to improve $T_g$ up to 120 °C. Thus, in association with the discussions in section 2.1.3 the consideration of enhancing $T_g$ is realized as one of the general criteria in the guidelines for designing novel small molecule organic HTMs in sMSC systems.

As discussion in section 2.1.7, the pore filling of HTMs into the mesoporous electrode appears to be a general limitation to device performance in the solution-processed sMSCs. For devices with high efficiencies, the percentage of pore filling close to unity is not necessary, however, it is advantageous if all light absorbers are located in direct contact with HTMs with consistency along the pathway of hole conduction for efficient regeneration and suppressed recombination reactions. Due to HTM infiltration problems and fast recombination the optimal film thickness of most efficient sMSCs is constrained to be considerably thin with the difficulty to reach unity LHE. Despite of the advantageous properties, incomplete pore filling of spiro-OMeTAD into the mesoporous electrodes were reported, which is attributed to its relatively low solubility in most commonly used organic solvents (300 mM in chlorobenzene) on account of its large molecular weight. In order to ensure that all dye molecules are located in contact with the HTM layer the film thickness of TiO$_2$ mesoporous electrode is required to be no more than 6 μm studied by PIA measurements. The pore filling of spiro-OMeTAD into the mesoporous TiO$_2$ film was evaluated by Snaith et al. from the thickness of residual HTM layer (also termed HTM overstanding or capping layer) after spin-coating procedure. McGehee et al. also determined the pore filling of spiro-OMeTAD with UV-vis spectroscopy by investigating the amount of redissolved HTM from the deposited HTM layer in devices, meanwhile the limitation of homogeneous infiltration of spiro-OMeTAD through the mesoporous film was observed at around 5 μm according to the results of X-ray photoelectron spectroscopy (XPS) profiling measurements. Both studies suggest that in films with thickness less than 3 μm pore filling of more than 60% can be obtained. Therefore methods to improve the pore filling of HTMs have been developed, among which melting HTM to infiltrate the pores appears to be a promising alternative scheme.

To cope with such a limitation McGehee et al. designed and synthesized two novel small molecule organic HTMs, namely AS37 and AS44 (Figure 3.1) with lower molecular weights, higher solubility and lower melting points ($T_m$). Similar to spiro-OMeTAD, methoxyl groups were introduced into the molecular structures of these two HTMs in order to enhance the solubility for efficient infiltration and to adjust the HOMO level for sufficient regeneration driving force. Based on the more electron-donating carbazole core structure, AS44 exhibits an impressive power conversion efficiency of 2.94% in a 2 μm thick Z907 sensitized sDSC. Moreover, AS44
even outperforms spiro-OMeTAD in a 6 μm thick device as the result of its better pore filling due to a higher solubility. The melting points of these two HTMs were determined at 106 °C and 132 °C respectively, which are slightly lower than the temperature of dye degradation providing the possibility for melting infiltration of HTMs in thicker devices. However, the hole-mobility of these two HTMs appears to be at the same order of magnitude as that of spiro-OMeTAD, which therefore does not improve the hole conduction.

As discussed in section 2.1.6, in organic HTMs positive charge carriers are transported between the neighbouring molecules and moieties subject to a hopping mechanism. The slow hole transport might increase the probability of charge recombination reactions and therefore lower the charge collection efficiency. The molecular structure of spiro-OMeTAD based on the twisted center of spiro-carbon significantly inhibits the intra- (between the two moieties connected via the spiro center) and inter-molecular π-π orbital coupling, which lowers the overall conjugated property of HTM layer resulting in a fairly low hole-mobility in the order of 10^{-5} cm²V⁻¹s⁻¹ in its pristine form and eventually leading to poor performance of hole conduction. As discussed in section 2.1.4, p-type dopants are necessarily employed to enhance the hole conductivity of HTM layer, especially the addition of Li-salt is essential for the spiro-OMeTAD based sMSCs to function.66-99 In addition, the relatively high synthetic cost of spiro-OMeTAD becomes another problem in terms of commercialization and up-scale production. Thus, the development of alternative HTMs overcoming these shortages becomes important in order to obtain cost-effective sMSC devices with better performance. In this thesis work, two low-cost organic HTMs featuring much higher hole-mobilities and solubilities, namely tris(para-anisyl)amine TPAA and N,N,N',N'-tetrakis(4-methoxyphenyl)benzidine MeO-TPD (Figure 3.1),150 have been studied as alternative hole conductors in sDSC devices.

By employing PIA and transient absorption spectroscopy, it was observed that TPAA is able to efficiently regenerate the oxidized K77 sensitizer84 in thick TiO₂ mesoporous film even more than 5 μm, which is attributed to the excellent pore filling due to its high solubility during spin-coating procedure in virtue of its low molecular weight.56,151 However, the photocurrent remains poor in spite of its high hole-mobility of 3 \cdot 10^{-3} cm²V⁻¹s⁻¹. Polymer HTM, P3HT in this case, with appropriate HOMO level with regard to that of TPAA was therefore added as a co-HTM to facilitate the hole conduction due to its high hole conductivity. The charge recombination was efficiently suppressed by such a co-HTM strategy resulting in an enhanced charge collection efficiency. The details regarding this work will be fully discussed in Chapter 5 (Paper II).

As a cost-effective alternative HTM to spiro-OMeTAD, MeO-TPD was studied in combination with sensitizer LEG4 in sDSC devices.152 The higher IPCE and photocurrent obtained from the MeO-TPD based device indicate that an efficient pore filling of this HTM into mesoporous electrode has been
achieved, which is attributed to its high solubility in organic solvents. As HTM in sDSCs MeO-TPD eventually outperforms spiro-OMeTAD in terms of faster charge transport, higher charge collection efficiency and overall power conversion efficiency due to the fact that the hole-mobility of MeO-TPD ($1 \cdot 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$)\textsuperscript{153-156} appears to be two orders of magnitude higher than that of spiro-OMeTAD. Meanwhile, it was discovered that an initial light soaking treatment at open circuit condition significantly improved the photovoltaic performance of MeO-TPD based sDSC devices due to the remarkably prolonged electron lifetime. According to these results a mechanism illuminating the evolution of photovoltaic performance depending on Li$^+$ ion migration towards the surface of TiO$_2$ nanoparticles under light soaking was suggested. The detailed discussion regarding to this work will be further specified in Chapter 5 (Paper III).

Both conjugated polymer and small molecule organic HTMs can be used for perovskite based sMSC devices. However, unlike sDSCs the film thickness of perovskite based sMSCs is generally thin in the range of 400 nm benefitting from the high LHE of perovskite absorbers, moreover the conductivity of perovskite itself appears to be considerably high on the order of $10^{-3}$ Scm$^{-1}$,\textsuperscript{157} the pore filling issue therefore no longer remains the primary limiting factor in this type of sMSCs. However, the presence of a HTM layer is still advantageous in the device, for example to avoid pinholes that might shunt the device. Thus, it is of particular importance to balance the series and shunt resistances in the perovskite based sMSCs.\textsuperscript{158}

Polymer HTM P3HT was employed in CH$_3$NH$_3$PbI$_3$ based sMSCs providing a power conversion efficiency of 4.5%.\textsuperscript{159} By blending P3HT with highly conducting multi-walled carbon nanotubes (MWCNTs), Dai et al. successfully enhanced the conductivity of HTM using P3HT/MWCNT composite by around one order of magnitude compared with pristine P3HT.\textsuperscript{160} Due to the $\pi-\pi$ coupling interaction P3HT firmly adsorbed on the MWCNT side walls to yield the interpenetrating composites with enhanced crystallinity and conductivity. The device based on such a mixed HTM therefore exhibits an enhanced efficiency of 6.5%. By employing a novel conjugated polymer HTM, PCBTDP (Figure 3.2), with high hole-mobility of $2 \cdot 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ and deep HOMO level of 5.4 eV, Qiu et al. achieved a strikingly high $V_{oc}$ of 1.15 V in association with CH$_3$NH$_3$PbBr$_3$ as light absorber meanwhile the power conversion efficiency of 5.6% with long-term stability was obtained in CH$_3$NH$_3$PbI$_3$ based sMSC devices.\textsuperscript{161}

In this thesis work, a small molecule organic HTM, 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH, Figure 3.2), was employed in comparison with spiro-OMeTAD and P3HT to investigate the influence of different HTMs on the charge recombination in CH$_3$NH$_3$PbI$_3$ based sMSC devices.\textsuperscript{159} It is observed that the electron lifetime ($\tau_e$) of theses devices using three different HTMs decreases by one order of magnitude in the sequence $\tau_{spiro-OMeTAD} > \tau_{P3HT} > \tau_{DEH}$ and the charge transport time is subject to the similar trend. Therefore the charge recombination in perovskite based sMSCs
highly depends on the nature of the HTMs, the details of which will be further discussed in Chapter 5 (Paper V).

Figure 3.2: Molecular structures of solution-processible organic HTMs used in perovskite based sMSCs, including DEH, H101, Py-A, Py-B, Py-C and PCBTDPP.

A novel small molecule organic HTM with cost-effective two-step synthetic route, 2,5-bis(4,4′-bis(methoxyphenyl)aminophen-4″-yl)-3,4-ethylenedioxythiophene (H101, Figure 3.2), has been developed based on the 3,4-ethylenedioxythiophene (EDOT) linked triphenylamine core. The power conversion efficiency of 13.8% was achieved with the addition of a p-type dopant. The decrease of the device performance over one week was found no more than 15% indicating H101 exhibits excellent potential as a low-cost
alternative HTM to spiro-OMeTAD for perovskite based sMSCs, which provides a new pathway for designing novel HTMs. Moreover, Seok et al. developed a series of pyrene/arylamine based derivatives (Py-A, Py-B, Py-C, Figure 3.2) with suitable electronic properties to function as HTM in perovskite based sMSCs.\textsuperscript{163} The HOMO/LUMO energy levels of these derivatives can be readily adjusted benefitting from the tunability by modifying the pyrene core with a variety of substituents. Among these HTMs, Py-C based device exhibits the best efficiency of 12.4%, which is comparable with that of spiro-OMeTAD based device. Although spiro-OMeTAD to date still remains as the most successful HTM in sMSC devices, the developments of novel alternatives appear essential in terms of acquiring new knowledge and opening promising pathways for designing highly efficient HTMs in sMSCs.

3.2 The Polymer HTMs prepared by \textit{in-situ} polymerization

When conducting polymers are used as HTMs in sMSCs, the pore filling issue often limits the device performance. There is an alternative method to spin-coating that circumvents such a problem, namely the \textit{in-situ} photoelectrochemical polymerization (PEP). In this approach, the dye-sensitized TiO\textsubscript{2} mesoporous electrode is immersed in the solvent, which contains the corresponding small organic precursors (monomers). Upon photo-excitation, the dye molecules inject electrons into the TiO\textsubscript{2} conduction band and then remain in their oxidized form. The oxidized sensitizers are subsequently reduced by taking electrons from dissolved monomers in surroundings, the process of which therefore triggers the \textit{in-situ} polymerization based on radical coupling between the active radicals of monomer, dimer and oligomer to eventually produce polymer HTMs directly inside the pores. Thus, high pore filling of HTMs into the mesoporous photoanode can be achieved after \textit{in-situ} polymerization with almost all dye molecules in direct contact with the HTM layer. This significantly improves the regeneration efficiency. The general operating mechanism of \textit{in-situ} PEP is schematically shown in Figure 3.3 using a three-electrode setup including dye-sensitized TiO\textsubscript{2} mesoporous film as working electrode (WE), reference electrode (RE, typically Ag/AgCl or calomel electrode) and counter-electrode (CE, typically stainless steel or Pt wire).

The PEP is typically applied as the most convenient method for \textit{in-situ} polymerization for sDSC applications, preferably in a three-electrode setup. The constant current (chronopotentiometry) or constant potential (chronoamperometry) is applied while the electrode potential is monitored vs. a suitable reference electrode to ensure it not to exceed the positive threshold, 0.4
V vs. standard hydrogen electrode (SHE) to avoid over-oxidation of the formed polymer.66,164-165

Figure 3.3: Schematic operating mechanism of in-situ PEP in a three-electrode set-up, where the dye-sensitized TiO₂ mesoporous film functions as the working electrode, the corresponding small organic precursors (monomers) are dissolved in solvent. The in-situ PEP process is initialized by the photo-induced oxidation of monomers.

Preparing HTM layer by in-situ polymerization in sDSC systems was initially introduced by Yanagida et al. using pyrrole as monomer precursor dissolved in MeCN, which produced 0.1% efficiency in a LiClO₄ doped sDSC device.166 Due to its promising performance as HTM in sDSCs in the presence of ionic constituents, the development of preparing PEDOT (Figure 3.4) by in-situ PEP has been intensively studied.167 This system has been further improved by investigating various hydrophobic sensitizers and p-type dopants.168-171 The performance of different organometallic sensitizers in sDSCs using PEP prepared polymer HTMs was summerized by Yanagida et al.172 Among different dopants, Li-TFSI was proven to provide the best performance by investigating the effects of different counter anions including the study how the anions containing perfluoroalkyl substituents influence the conductivity of PEDOT.173 To date the performance of sDSC devices using PEP prepared HTMs has been improved to 7.1% by Liu et al. using an organic sensitizer D205 with doped PEDOT produce by in-situ PEP from 2,2′-bis-(3,4-ethylenedioxy)thiophene (bis-EDOT, Figure 3.4) monomer dissolved in MeCN.174
However, due to the solubility limitation of the precursor compounds including monomers and oligomers, the previous development of \textit{in-situ} PEP technology was mainly performed in organic solvents, typically MeCN. This is unfortunately unfavourable in terms of environmental concerns and large-scale production costs. Moreover, the oxidation onset of most organic precursor compounds lies in relatively high potential regions during the \textit{in-situ} PEP process, which significantly narrows the choice of applicable dye/precursor couples where the photo-oxidized sensitizer can function as oxidant with sufficient driving force to readily trigger the HTM deposition by \textit{in-situ} PEP. Apart from the limited choice of materials, high oxidation potential might result in overoxidation of the prepared polymer HTMs and therefore lower the device performance. However, the aqueous media containing surfactants or cyclodextrins have been proven to provide notable capability of efficiently dissolving most organic hydrophobic precursors, meanwhile decreasing their oxidation potential values during polymerization to avoid overoxidation effects.\textsuperscript{175-179} Therefore surfactant modified aqueous media can be effectively used as alternative media to organic solvents for \textit{in-situ} PEP.
In this thesis (Paper IV), a new method was developed to perform *in-situ* PEP from aqueous media containing the organic precursor *bis*-EDOT in the presence of a surfactant, in this case TritonX-100. As shown in Figure 3.5 the micelles encapsulate the organic monomers to efficiently increase their solubility in aqueous electrolyte. When these micelles diffuse to the vicinity of the photo-oxidized sensitizers encapsulated monomers are released and subsequently oxidized to trigger the radical polymerization. Competitive photovoltaic performance was achieved in sDSC devices using aqueous-phase polymerized PEDOT as HTM. The influence of different types of electrolyte media (aqueous-phase and organic-phase) and different sensitizers on device performance was investigated. The detailed discussion regarding to this work will be further specified in Chapter 5 (Paper IV).
4. Methods

4.1 Preparation of components and sMSC devices

The specific device fabrication methods are presented in each corresponding paper while in this chapter the general methods for preparing components and sMSC devices will be introduced including the fabrication of sDSC devices, the preparation of the polymer HTM PEDOT by in-situ PEP, and the preparation of perovskite compounds and sMSC devices.

4.1.1 Fabrication of sDSC devices

The fabrication of sDSC devices was carried out according to the following sequential procedures: First of all, a compact TiO$_2$ blocking layer was deposited onto the pre-cleaned FTO-coated glass substrate (purchased from Pilkington, 15 Ω/□, 2.3 mm thick, high transparency) on hotplate at 450 °C by spray pyrolysis. In order to achieve the pinhole-free TiO$_2$ blocking layer, the thickness was controlled by 10 spray cycles as standard parameter using an air brush vertically spraying from above in a distance of approximately 5 cm with 30 s interval between each cycles. The solution containing 0.2 M Ti-isopropoxide and 2 M acetylacetone in isopropanol was applied as precursor for the formation of compact TiO$_2$ by pyrolysis during spraying procedure.

Afterwards mesoporous TiO$_2$ films were prepared above the blocking layer by spin-coating a colloidal TiO$_2$ paste (Dyesol DSL 18NR-T) consisting of nanoparticles with an average diameter of 20 nm diluted with terpineol (46.2% in weight ratio, Sigma-Aldrich). In order to obtain the mesoporous TiO$_2$ film with thickness around 2.2 μm, as measured with DekTak profilometer and SEM, the spin-coating rate of 2400 rpm for 30 s was tested and adopted. After sintering the TiO$_2$ film on the hotplate at 500 °C for 30 min for phase transition into anatase, the film was cooled to room temperature in ambient atmosphere and then immersed in 0.02 M aqueous TiCl$_4$ at 70 °C for 30 min in order to achieve the sufficient inter-particle connection between the TiO$_2$ nanoparticles for efficient charge carrier transport. Subsequently a second sintering step with same program was performed after rinsing the films with deionized water.

To adsorb the sensitizers onto the surface of mesoporous TiO$_2$ electrode, dye-sensitization was performed by immersing the annealed warm TiO$_2$ films into the 0.5 mM dye solution in organic solvents, usually MeCN, for 18 h to allow the high surface coverage or dye loading to be achieved for efficient
light harvesting. Afterwards the sensitized films were rinsed with deionized water and the UV-vis absorption spectra of the samples were recorded for the comparison with IPCE spectra in future.

For control samples with spiro-OMeTAD as HTM, a solution of 150 mM spiro-OMeTAD (Lumtech) (213 mg/mL), 120 mM t-BP (96%, Sigma-Aldrich) and 20 mM Li-TFSI (99.95%, Sigma-Aldrich) in chlorobenzene was prepared in an argon glovebox and applied to the films by leaving the solution to penetrate into the films for 30 s prior to spin-coating for 30 s at 2000 rpm. For samples based on other solution-processible HTMs including P3HT, TPAA, mixture of TPAA and P3HT, MeO-TPD, the solution of close to saturated HTM concentration with varied concentrations of 4-tert-butylpyridine and Li-TFSI in chlorobenzene was prepared respectively in an argon glovebox prior to spin-coating according to the similar procedure discussed above. The infiltration of HTM solutions into the mesoporous electrode was carried out by capillary force. The penetration depth and pore filling are therefore primarily influenced by the concentration and viscosity of the HTM solutions as well as the soaking time. The spin-coating technique was employed in this step to remove the excess HTM solution and to form a smooth overstanding residual layer of HTM with high uniformity on the top of mesoporous TiO$_2$ film. As discussed in previous chapters, the pore filling of HTMs significantly influences the regeneration and charge collection efficiencies. Moreover the residual HTM layer is essentially crucial for separating the counter-electrode and the photo-anode to prohibit the charge recombination. Therefore this procedure of applying the HTM layer becomes a significant limiting factor to the device performance during the fabrication processes of sDSC devices.

Finally, to complete the device, an Ag (Sigma-Aldrich, ≥ 99.99% trace metals basis) contact with thickness around 200 nm was deposited onto the organic semiconductor HTM layer by thermal physical vapor deposition (PVD) in a vacuum chamber (Leica EM MED020) with a base pressure of around 10^{-5} mbar.

4.1.2 Preparation of PEDOT as HTM by in-situ PEP

The three-electrode setup was employed for in-situ PEP. The dye-sensitized mesoporous TiO$_2$ films were employed as working electrodes. The Ag/AgCl (3 M NaCl) electrode was employed as the reference electrode while the stainless steel was used as the counter electrode. For comparison between in-situ PEP from organic or aqueous solution, two alternative electrolytes were prepared for in-situ PEP of bis-EDOT monomer: (i) the organic electrolyte consisting of 10 mM bis-EDOT and 0.1 M Li-TFSI dissolved in MeCN; (ii) the aqueous micellar electrolyte containing bis-EDOT with saturated concentration (solubility below 1 mM), 2% v/v MeCN, 0.1 M Li-TFSI and 50 mM TritonX-100 as solubilizing medium in the aqueous solution.

To photo-oxidize the sensitizers, the illumination with white light was ex-
posed through the backside (glass side) of the dye-sensitized TiO\textsubscript{2} films generated by an LED lamp (ELFA Distrelec, Light Injector, white, 6000 K–6\textdegree, 3 W, 4.5 V, 700 mA) as the excitation light source. In order to achieve the uniform conducting polymer layer inside the pores and the suitable over-standing layer with optimized thickness, the chronopotentiometry was performed with optimized values of duration and constant current through the system during \textit{in-situ} PEP for different combinations of \textit{bis}-EDOT monomer with a diversity of dye/TiO\textsubscript{2} electrodes respectively. The detailed parameters with regard to the duration and constant current applied during \textit{in-situ} PEP can be found in the experimental sections of the corresponding paper (Chapter 5, Paper IV) included in this thesis work.

During the \textit{in-situ} PEP the electrode potential was monitored vs. the reference electrode to ensure it not to exceed the positive potential limit, 0.4 V vs. SHE in order to prevent over-oxidation of both the deposited conducting polymer and the TiO\textsubscript{2} blocking layer. The former might lead to the decrease in the conductivity of the polymer HTM while the latter results in the exposure of bare FTO to electrolyte shunting the device due to the damage of the TiO\textsubscript{2} blocking layer. Once the \textit{in-situ} PEP was finished, the remaining electrolyte was rinsed off the PEDOT-filled dye-sensitized mesoporous TiO\textsubscript{2} films with ethanol. Subsequently the films were dried by N\textsubscript{2} flow prior to the deposition of Ag counter-electrode.

4.1.3 Synthesis of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite compound

The perovskite compound CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} was synthesized according to the procedure reported previously.\textsuperscript{65,67} In general, a hydroiodic acid (30 mL, 57 wt.% in water, Sigma-Aldrich) was slowly mixed with methylamine (27.8 mL, 0.273 mol, 40% in methanol, TCI) under magnetic stirring at 0 °C for 2 h. The resulting solution was then dried by evaporation yielding synthesized compound CH\textsubscript{3}NH\textsubscript{3}I. Subsequently the custom-synthesized CH\textsubscript{3}NH\textsubscript{3}I was mixed with PbI\textsubscript{2} in equal molar ratio in \textgamma-butyrolactone under stirring at 60 °C overnight to provide the solution of target perovskite compound CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. The CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} solution was then filtered prior to use.

4.1.4 Fabrication of perovskite based sMSC devices

Similar to the fabrication procedures of sDSC devices, perovskite based sMSC was also built on the FTO glass substrate coated with TiO\textsubscript{2} blocking layer (produced by spray pyrolysis). The major difference lies in the replacement of dye molecules by perovskite absorbers and the relatively thinner mesoporous TiO\textsubscript{2} film. The mesoporous TiO\textsubscript{2} layer with thickness around 500 nm was spin-coated onto the blocking layer and sintered at 500 °C for 30 min in ambient atmosphere. The resulting film was then spin-coated with perovskite precursor solution containing 40 wt% CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} at 1500 RPM for 30 s in dehumidified atmosphere followed by heating treatment at 100 °C
for 20 min in air. For comparison, three different HTMs, 500 mM DEH, 170 mM spiro-OMeTAD and 20 mg/mL P3HT were applied respectively by spin-coating at 4000 rpm from chlorobenzene solution containing 64 mM Li-TFSI and 198 mM \( \tau \)-BP. Eventually a 200 nm thick Ag counter-electrode was deposited onto the overstanding HTM layer to complete the device by PVD similar to the previous discussion.

4.2 Characterization of components

The variety of methods used in this thesis work to characterize the sMSC components will be briefly introduced in this section including UV-visible spectroscopy (UV-vis) for measuring spectral properties of sensitizers and HTMs; cyclic voltammetry (CV) for determining the electronic energy levels of sensitizers and monomers; photo-induced absorption spectroscopy (PIA) for studying the regeneration of sensitizers; nanosecond transient absorption spectroscopy (TAS) for investigating the kinetics of regeneration and recombination reactions; space charge limited current measurement (SCLC) for determining the hole-mobility of HTMs; scanning electron microscope measurements were performed to investigate the cross-sectional surface morphology of sMSC substrates.

4.2.1 UV-visible spectroscopy

UV-visible absorption spectra of sensitized TiO\(_2\) films and dye solutions were recorded on a HR-2000 Ocean Optics fiber optics spectrophotometer. A normal quartz cuvette (1 cm path length) was used for the measurements of dye solutions. The UV-vis spectra characterize the spectral properties of sensitizers such as transmittance \( T \), absorbance \( A(\lambda) \) and extinction coefficient \( \varepsilon(\lambda) \), which therefore becomes one of the most commonly used techniques for characterization of light absorbers. The transmittance is defined in Equation 4.1 shown as below, where \( I \) stands for the transmitted light intensity while \( I_0 \) denotes the incident light intensity.

\[
T = \frac{I}{I_0} \tag{4.1}
\]

As exhibited in Equation 4.2, the absorbance at a specific wavelength can be described as a function of transmittance or extinction coefficient.

\[
A(\lambda) = -\log T(\lambda) = cI\varepsilon(\lambda) \tag{4.2}
\]

where the right-hand part of the equation is defined by Lambert-Beer’s law, \( c \) stands for the concentration of the species in solution and \( l \) denotes the optical path length. The absorbance of a sensitizer becomes a significant
parameter due to its correlation with LHE as defined in Equation 2.4, which directly characterizes the light harvesting capability of the sensitizers and therefore influences the IPCE.

4.2.2 Electrochemistry

In this thesis work, electrochemical methods were mainly performed on a CH Instruments 660 potentiostat with a three-electrode set-up to characterize the electronic properties of the sMSC components, among which cyclic voltammetry (CV) was used to determine the oxidation potentials of sensitizers and monomers. In this method, the voltage at the WE is linearly swept back and forth between two set potential values at a certain scan rate while the current is monitored. In electrochemical measurements, there are two major contributions to the current through the system, namely the charging processes (non-Faradaic) and the charge transfer reactions (Faradaic), where the latter correspond to the oxidation or reduction processes of the analytes at the WE. In general, the charging current can be described as a linear function of the scan rate while the faradaic current depends on the square root of the scan rate, if the transport of analytes is controlled by diffusion.\(^{181}\)

![Figure 4.1: Cyclic voltammetry of ferrocene measured by scanning the applied potential between 0 V and 7 V at a scan rate of 50 mVs\(^{-1}\). A supporting electrolyte containing 0.1 M Li-TFSI in MeCN was used.](image)

Figure 4.1 shows a cyclic voltammogram of ferrocene measured by scanning the applied potential between 0 V and 0.7 V at a scan rate of 50 mVs\(^{-1}\), where the mesoporous TiO\(_2\)/FTO film without blocking layer was used as working electrode. Ag/AgCl (3 M NaCl) electrode was used as reference electrode and stainless steel grid was used as the counter-electrode. The electrolyte solution consists of 100 mM Li-TFSI in MeCN. This measurement was performed as the internal calibration to relate the reference electrode to the redox potential of the ferrocene/ferrocenium couple (Fc/Fc\(^+\)). Electro-
chemical measurements can also be combined with UV-vis spectroscopy to simultaneously monitor the changes in absorption spectra during the electrochemical processes when the analytes are electrochemically oxidized or reduced. This combination of methods is termed as spectroelectrochemistry, which can be used, for instance, to determine the extinction coefficient of analytes.

4.2.3 Photo-induced absorption spectroscopy

Photo-induced absorption spectroscopy was employed to qualitatively investigate the regeneration of light absorbers under the operating conditions of sMSC devices. PIA spectra were recorded on the custom-designed setup as reported previously. White probe light is generated by a 20 W tungsten-halogen lamp. For excitation of the analyte molecules, a square-wave modulated (on-off) pump-light source is superimposed with the probe light, which is either a blue LED (Luxeon Star 1 W, Royal Blue, 460 nm), a green laser (Lasermate GML 532-100FLE, 532 nm), or a red laser (Coherent Model #31-1050, 635 nm). The transmitted probe light is then focused onto a monochromator (Action Research Corporation SP-150) and detected by a UV enhanced silicon photodiode connected to a current amplifier and lock-in amplifier (Stanford Research System models SR570 and SR830, respectively). The PIA setup has been described in details elsewhere.

4.2.4 Nanosecond transient absorption spectroscopy

Transient absorption spectroscopy is a time-resolved spectroscopic method, which was performed to provide quantitative information of regeneration kinetics as the complementary analysis to PIA spectra. For the excitation of analytes, a nanosecond laser (Nd:YAG, Continuum Surelight II, repetition rate: 10 Hz, pulse length: 10 ns, 20 mJ pulse\(^{-1}\) cm\(^{-2}\)) was used in combination with an OPO (Continuum Surelight) pump pulses (attenuated to 0.1 mJ pulse\(^{-1}\) cm\(^{-2}\)) at 625 nm. A near-IR LED (Osram SHF 484, \(\lambda_{\text{max}}\) 880 nm, FWHM 80 nm) was used as the probe light focused onto the sample. The kinetic traces of oxidized species were measured with an amplified Si photodiode (Thorlabs PMA10A) as the detector in association with a cutoff filter (RG 715) placed in front to avoid stray light from the laser.

For example, Figure 4.2 shows the time-resolved nanosecond TAS kinetic traces of sensitizer K77 with or without HTMs on mesoporous TiO\(_2\) electrodes. The detected signal at 880 nm is mainly derived from the absorption of oxidized K77. Therefore the decay rate of this signal indicates the regeneration kinetics of the oxidized K77 in the presence of HTM or the recombination kinetics of free charge carriers at dye/TiO\(_2\) interface in the absence of HTM.
4.2.5 Space charge limited current measurement

In order to determine the hole-mobility of PEDOT prepared by *in-situ* PEP, space charge limited current measurement was performed between two deposited Ag electrodes on the PEDOT/dye/TiO\(_2\) substrates in the dark. The electrical data were recorded on a computer-controlled digital sourcemeter (Keithley Model 2400) with the scan direction from -2.5 V to +2.5V at 50 mVs\(^{-1}\). The distance and area between the two Ag electrodes were 2 mm and 0.1 cm\(^2\) respectively.

In this measurement, the current flowing through the device will be limited by the space-charge build-up within the film when the contact at HTM/dye interface is ohmic without unfilled trap states. The current-voltage ($J$-$V$) characteristics in thin film ($L$) can be described by the following equation:

$$J = \frac{2}{\pi} \mu \varepsilon_r \varepsilon_0 \frac{V^2}{L^2}$$  \hspace{1cm} (4.3)

where $J$ stands for the current density flowing through the film, $\mu$ denotes the hole-mobility of HTM, $\varepsilon_r$ is the dielectric constant of the material (normally 3 for organic semiconductors), $\varepsilon_0$ is the permittivity of the vacuum, $V$ is the voltage applied across the two Ag electrodes and $L$ denotes the distance of 2 mm between two Ag electrodes. According to Equation 4.3, the hole-mobility therefore can be extracted from the slope when the square root of current density is plotted vs. voltage.

4.2.6 Scanning electron microscopy

Scanning electron microscope measurements (Zeiss LEO1550 high resolution SEM) were performed to investigate the surface morphology of sMSC substrates. The cross-sectional topography was visualized by SEM images to qualitatively study the pore filling of HTMs. Samples were scribed on the substrate (glass) side and cracked into small portions prior to the acquisition.
of SEM images. The acceleration voltage (EHT) was 5 or 10 kV and the working distance (WD) was ranged from 4 to 13.5 mm. The magnification in the range from 25 000 to 200 000× was adopted. The thickness of the over-standing layer of HTMs on top of the mesoporous TiO$_2$ electrode was estimated by zooming into the top-most region of the films.

4.3 Characterization of complete devices

A variety of techniques were employed to characterize the complete sMSC devices including current-voltage $I$-$V$ measurement for determining the critical parameters of the solar cells, such as power conversion efficiency $\eta$, fill factor $FF$, short circuit current density $J_{sc}$ and open circuit voltage $V_{oc}$; incident photon to current conversion efficiency IPCE for investigating how efficiently the incident photon can be converted into photocurrent output by solar cells; photocurrent and voltage decay measurement for estimating the electron lifetime and transport time to study the kinetics of charge recombination and electron transport through the mesoporous electrode.

4.3.1 Current-voltage measurement

The current-voltage characteristics ($I$-$V$ curves) were measured with a solar simulator using the light source from a 300 W collimated xenon lamp (Newport) calibrated with the light intensity to 1000 Wm$^{-2}$ at 1.5 AM Global condition by a certified silicon solar cell (Fraunhofer ISE). The electrical data were recorded on a computer-controlled digital sourcemeter (Keithley Model 2400) with the scan direction from open-circuit to short-circuit at scan rate in the range from 11.9 to 50 mV/s. During the measurements the sMSC devices were masked with an aperture area of 0.20 cm$^2$ exposed under illumination.

As shown in Figure 4.3, the photocurrent density is recorded along the scan of voltage in the direction from $V_{oc}$ to 0 V to provide an $I$-$V$ curve of a D35 sensitized sDSC with a 4.7% $\eta$ under 1 sun illumination. Where the $V_{oc}$ is determined as the measured potential at open circuit condition when the photocurrent density equals to 0 Acm$^{-2}$ and the $J_{sc}$ is determined as the measured photocurrent density at short circuit when the photovoltage equals to 0 V. Along the $I$-$V$ curve, where the product of the photocurrent density and voltage reaches its maximum value, the maximum power the device can provide can be found as $P_{max}$ with its corresponding photocurrent density $J_{max}$ and photovoltage $V_{max}$. The overall power conversion efficiency of the sMSC device is therefore defined as the ratio of the maximum power generated over the power of the incident light ($P_{in} = 1000$ Wm$^{-2}$, 1.5 AM G), according to the following equation:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc}V_{oc}FF}{P_{in}}$$

(4.4)
where the \( FF \) stands for the fill factor defined in Equation 4.5 as a parameter to evaluate the deviation of the measured device efficiency from the theoretical maximum power output of the device.

\[
FF = \frac{I_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}}
\]  

(4.5)

The higher the \( FF \), the device efficiency appears to be closer to its potential theoretical maximum, the better photovoltaic performance the sMSC device provides.

![Figure 4.3: I-V characteristics of a D35 sensitized sDSC device measured under 1 sun illumination (black trace with square) and in the dark (red trace with circle), where the maximum power point \( P_{\text{max}} \), short circuit current density \( J_{\text{sc}} \) and open circuit voltage \( V_{\text{oc}} \) are marked to illustrate the calculations of power conversion efficiency \( \eta \) and fill factor.](image)

The \( I-V \) curve can also be measured in the dark referred to as the dark current curve, which to some extent provides the information about charge recombination reaction to oxidized HTM species due to the absence of the oxidized sensitizers in the dark. As illustrated in Figure 4.3, the red trace with circle presents the dark current curve of the D35 sensitized sDSC device, where the dark current density remains negligible in large voltage range from 0 to 0.6 V. This indicates that the TiO\(_2\) blocking layer functions well and the mesoporous TiO\(_2\) surface is highly protected by the dye layer, which therefore efficiently prohibits the dark current through the system with sufficiently high shunt resistance across the device so that this device exhibits high photovoltaic performance since the recombination to oxidized HTM species is efficiently suppressed.
4.3.2 Incident photon to current conversion efficiency

The Incident photon to current conversion efficiency (IPCE), also termed as the external quantum efficiency (EQE), indicates how efficiently the incoming photons at a specific wavelength are converted into photocurrent. In the IPCE measurement, the device is exposed to illumination by monochromatic light with known photon flux $\Phi(\lambda)$. The IPCE spectrum is obtained by scanning through each spectral wavelength meanwhile recording the photocurrent output simultaneously. The IPCE measurement is usually performed at short circuit conditions. However, it can also be measured at an applied potential or under a bias white light. In this thesis work, the IPCE spectra were mainly measured at short circuit conditions recorded on a computer-controlled setup consisting of a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a multimeter (Keithley 2700). The equipment was calibrated with a certified silicon diode (Fraunhofer ISE) prior to measurements. All sMSC devices were illuminated from the substrate (glass) side with an aperture area of 0.16 cm$^2$. Figure 4.4 shows an example of IPCE spectrum of a sDSC with D35 as sensitizer.

![IPCE spectrum of a D35 sensitized sDSC device.](image)

The magnitude of the IPCE spectrum depends on how much incident photons are absorbed and converted into electrons by the sMSC devices. Therefore the IPCE is determined in Equation 4.6 by the light harvesting efficiency $LHE$, the injection efficiency $\varphi_{inj}$, the regeneration efficiency $\varphi_{reg}$ and the charge collection efficiency $\varphi_{cc}$.

$$IPCE = LHE \varphi_{inj} \varphi_{reg} \varphi_{cc}$$

(4.6)

The integrated IPCE photocurrent can be calculated by integrating over the product of the IPCE and the standard solar irradiance spectrum (Equation
where \( \Phi(\lambda) \) denotes the photon flux at a specific wavelength (1.5 AM G). In some cases, the absorbed photon to current conversion efficiency (APCE), also termed as the internal quantum efficiency (IQE), is extracted from IPCE according to Equation 4.8 to quantitatively discuss the contributions to the photocurrent attributed to the injection, regeneration and charge collection efficiencies.

\[
APCE = \frac{IPCE}{LHE} = \varphi_{inj} \varphi_{reg} \varphi_{cc} \tag{4.8}
\]

### 4.3.3 Photocurrent decay and voltage decay measurements

As discussed in previous chapters, the \( V_{oc} \) in sMSC device can be determined by the difference between the Fermi level in mesoporous TiO\(_2\) electrode \( (E_{F,n}) \) and the Fermi level in HTM \( (E_{F,HTM}) \) according to Equation 4.9.

\[
eV_{oc} = E_{F,n} - E_{F,HTM} \tag{4.9}
\]

At thermodynamic equilibrium in the dark, \( E_{F,n} \) equals to \( E_{F,HTM} \) providing a zero \( V_{oc} \), while under illumination \( E_{F,n} \) is shifted upwards by increasing the charge density in TiO\(_2\) conduction band according to the following equation:

\[
E_{F,n} = E_{CB} + k_BT \ln \frac{n_{CB}}{N_{CB}} \tag{4.10}
\]

where \( E_{CB} \) is the conduction band edge, \( n_{CB} \) denotes the electron density in the conduction band and \( N_{CB} \) designates the density of states in the conduction band. When the light intensity increases, the \( E_{F,HTM} \) is relatively stable close to the \( E_{HOMO} \) of the HTM due to the high doping concentration while \( E_{F,n} \) is shifted upwards since \( n_{CB} \) increases with light intensity, therefore the photovoltage increases with the increased light intensity. Moreover, according to Equation 4.7, the photocurrent also depends on the incident light intensity. Thus, the photovoltage (at open circuit conditions) and current (at short circuit conditions) transients caused by a small modulated square wave pulse on the light intensity of illumination can be measured to investigate the kinetics of charge recombination and transport. These transient signals can be fitted with single exponential decay functions due to the small amplitude of the modulations (Equation 4.11 and 4.12).

\[
V(t) = V_{oc} + \Delta V e^{-t/\tau_n} \tag{4.11}
\]
\[ J(t) = J_{sc} + \Delta J e^{-t/\tau_{resp}} \] (4.12)

where \( \Delta V \) and \( \Delta J \) denote the voltage and current differences from the small modulated light intensity respectively while \( t \) is the time. From these measurements, the two critical time constants, the electron lifetime \( \tau_n \) (described in Equation 2.9 characterizing how fast the recombination reactions occur) and the response time of photocurrent decay \( \tau_{resp} \) can be determined. The latter corresponds to the depletion of free electrons in TiO$_2$ conduction band at short circuit conditions, which therefore is attributed to two processes: the electron transport to external circuit and the charge recombination to either oxidized light absorbers or oxidized HTMs. Thus the electron transport time \( \tau_{trans} \) can be extracted from \( \tau_{resp} \) according to Equation 4.13 since the time constant corresponding to recombination \( \tau_n \) is measured independently.\textsuperscript{53}

\[ \frac{1}{\tau_{trans}} = \frac{1}{\tau_{resp}} - \frac{1}{\tau_n} \] (4.13)

In general, \( \tau_n \) exhibits a reverse dependence on the light intensity of illumination due to the effect that \( n_{CB} \) increases along the rise of light intensity resulting in the increased charge recombination. Once \( \tau_n \) and \( \tau_{trans} \) are determined, charge collection efficiency \( \varphi_{cc} \) can be calculated according to Equation 2.7 where the rate constants can be rewritten as the reciprocal of these two time constants.\textsuperscript{24} Hence, due to their direct correlation with transport and recombination of charge carriers, \( \tau_n \) and \( \tau_{trans} \) become the two most significant parameters to discuss the photovoltaic performance of sMSC devices in terms of charge collection efficiency.

In this thesis work, the measurements of transient photocurrent and voltage decay as a function of light intensity were performed with the custom-designed “toolbox setup” using a white LED (Luxeon Star 1W) to provide the base light intensity. The transient voltage and current responses of the sMSC devices were recorded by using a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems RS570) and a custom-designed electromagnetic switching system. By superimposing the base light with a small square wave modulation (< 10%, 0.5 Hz), the transient signals of photovoltage and current decay were recorded and subsequently fitted with first-order exponential functions in order to extract the three time constants.
5. Results

5.1 Comparing spiro-OMeTAD and P3HT in sDSC (Paper I)

Solar cells based on organic conducting polymer HTM in combination with inorganic mesoporous TiO₂ electrodes are called hybrid solar cells, which has shown promising results recently. As discussed in previous chapters, the low hole-mobility of spiro-OMeTAD becomes a limiting factor on device performance. The conjugated polymer P3HT (Figure 1.6) with high conductivity was therefore tested in sDSC as alternative HTM. Two organic sensitizers were employed including D35 with one anchor unit and M3 with two anchor groups (Figure 2.2). Due to the molecular structure with two anchor units, larger surface occupation of M3 dye molecule is expected resulting in a relatively low dye loading in the mesoporous film compared to D35. The M3 sensitized devices therefore showed similar absorption and IPCE spectra compared with D35 sensitized devices despite that the extinction coefficient of M3 is higher than that of D35.

![Figure 5.1: I-V curves of sDSCs with four different combinations of two dyes and two HTMs: a) D35 sensitized sDSC with spiro-OMeTAD as HTM (black trace with square); b) M3 sensitized sDSC with spiro-OMeTAD as HTM (red trace with circle); c) D35 sensitized sDSC with P3HT as HTM (blue trace with up-triangle); d) M3 sensitized sDSC with P3HT as HTM (green trace with down-triangle).]

5.6
As shown in Figure 5.1, the photovoltaic performance of the sDSCs using spiro-OMeTAD exhibited competitive results independent on the different properties of the two sensitizers (4.7% \( \eta \) for D35 and 4.9% \( \eta \) for M3) while the P3HT based devices showed remarkable difference in photovoltaic performance highly dependent on the sensitizers (3.2% \( \eta \) for D35 and 0.5% \( \eta \) for M3).\(^{56}\) As the four devices exhibited similar \( V_{oc} \) the difference can be primarily attributed to photocurrent. In the two devices using P3HT as HTM, such a difference becomes even more obvious that the photocurrent generated by D35 based device was as twice great as that of M3 based device. According to Equation 4.6 and 4.7, the difference in photocurrent could probably be derived from the difference in regeneration and charge collection efficiencies since the injection is usually efficient for these organic dyes and the LHE appears to be quite similar as observed in absorption spectra of these four devices.

In order to study the photocurrent difference observed in \( I-V \) measurements, PIA was performed to investigate the regeneration of oxidized dye species by these two different HTMs. The PIA spectra are compared to the extinction coefficients of electrochemically oxidized dye molecules and HTMs obtained by spectroelectrochemistry measurements, from which the concen-
trations of the different species could be determined. As shown in Figure 5.2a, the peak at 710 nm is attributed to the absorption of oxidized spiro-OMeTAD and the negative signal below 600 nm is assigned to the Stark effect on the absorption of sensitizers. The PIA spectra of both D35 and M3 sensitized films with spiro-OMeTAD were well matched with the absorption of the oxidized spiro-OMeTAD indicating that no contribution of oxidized dye species was observed. Therefore it can be assumed that the regeneration of both oxidized dye molecules is efficient in the devices using spiro-OMeTAD as HTM.

However, the PIA spectra of both D35 and M3 sensitized TiO$_2$ films with P3HT as HTM showed inconsistency with the extinction coefficient spectrum of oxidized P3HT minus ground state P3HT. It was also noticed that the difference between PIA and extinction coefficient spectra of P3HT can be efficiently reduced by adding the contribution from the extinction coefficient spectra of oxidized dye minus ground state dye in both cases, where the improvement appeared to be greater in M3 sensitized films. This revealed that the presence of non-regenerated dye molecules was expected in both cases and the oxidized M3 species were regenerated even less efficiently by P3HT, which was further proven by the concentrations of oxidized dye and P3HT molecules calculated by combining the PIA and spectroelectrochemical data.

The cross-sectional SEM images suggested the presence of less than 200 nm overstanding HTM layer for devices using both HTMs. However, due to its large spatial size and molecular weight the pore filling of P3HT was much lower than spiro-OMeTAD indicated by its low absorption spectra but high extinction coefficient, which implied that only part of the dye molecules were located in contact with HTM in P3HT based sDSC devices. Therefore it was assumed that those oxidized dye molecules in no contact with P3HT might be regenerated by the dye-dye hole hopping mechanism through the dye layer itself. Such a mechanism was previously demonstrated for phosphonated triarylamine molecules adsorbed onto the surface of mesoporous metaloxide films.

In order to investigate the dye-dye hole conduction by these two triarylamine based sensitizers, electrochemical measurements were respectively performed on the D35 or M3 sensitized mesoporous TiO$_2$ films without blocking layer. The evolution of charges was recorded as a function of square root of time after stepping the applied potential from negative to the oxidation potential of each dye. Such a plot should be linear if the electrochemical reaction is diffusion controlled, where the gradient is determined by the square root of the diffusion coefficient and the surface concentration of dye molecules. The rate of charge evolution appeared to be one third higher for D35 than M3 at its maximum, which indicates that the dye-dye hole hopping occurs better in D35 than M3 and therefore partially contributes to the regeneration of oxidized dye species in the absence of HTM.
In this paper the influence of two different types of HTMs on sDSC photovoltaic performance was studied in combination with two different organic sensitizers D35 and M3. The PIA spectra in association with spectroelectrochemical data suggested that insufficient regeneration of oxidized dye species was observed in P3HT based devices. Less sufficient pore filling of P3HT into the mesoporous electrode compared with spiro-OMeTAD was identified as the primary reason for their worse device performance. Moreover, it was noticed that the dye-dye hole conduction occurs in the absence of HTM and appears to be more efficient through the dye layer of D35 than M3 rationalizing the better performance of D35 over M3 in P3HT based devices. Therefore the dye-dye hole conduction could be of significant importance for optimizing the energy conversion efficiency in such a hybrid system with conjugated polymers as HTM.

5.2 Co-HTM strategy to enhance photocurrent (Paper II)

It has been realized in previous study (Paper I) that the regeneration of oxidized organic sensitizers remains inefficient by conjugated polymer P3HT due to its incomplete pore filling in sDSC devices. Similar results were also obtained by PIA measurements for the ruthenium sensitizer K77. The left panel of Figure 5.3 shows the PIA spectra of K77 sensitized TiO$_2$ film with thickness of 5.4 $\mu$m with or without P3HT.$^{188}$ The signal at 780 nm is assigned to the absorption of oxidized K77 ($K77^+$) similar to that of N719 reported elsewhere.$^{151}$ When P3HT was applied as HTM the PIA signal of $K77^+$ was only reduced by a small portion suggesting insufficient regeneration.

Figure 5.3: On the left panel, PIA spectra with a 532 nm pump light of TiO$_2$/K77, TiO$_2$/K77/TPAA, TiO$_2$/K77/P3HT and TiO$_2$/P3HT samples, a model PIA spectrum of TiO$_2$/K77/P3HT is also included by the addition of PIA spectra of TiO$_2$/K77 and TiO$_2$/P3HT. On the right panel, the PIA spectra of TiO$_2$/K77 and TiO$_2$/K77/(TPAA+P3HT) samples measured with a pump light at 632 nm.$^{188}$
In order to cope with the pore filling limitation, instead of P3HT a small molecule organic HTM TPAA (Figure 3.1) with low absorption in visible spectral region and high hole-mobility of $3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was employed in combination with K77 sensitizer to construct the sDSCs. The signal of K77$^+$ is considerably reduced in the presence of TPAA while the absorption peak of oxidized TPAA at 740 nm emerges instead, which indicates that as the HTM TPAA completely infiltrates into the thick mesoporous electrode and regenerates the oxidized K77 in a highly efficient manner. Such an observation was further confirmed by the nanosecond TAS spectra, where the sample was excited at 625 nm and probed at 880 nm to avoid the contribution from the absorption of TPAA and TPAA$^+$ species, and therefore the kinetics of K77$^+$ can be followed.

Figure 5.4: Nanosecond TAS spectra of TiO$_2$/K77, TiO$_2$/K77/TPAA and TiO$_2$/K77/(TPAA+P3HT) samples measured with pump wavelength at 625 nm and probe wavelength at 880 nm.$^{188}$

As shown in Figure 5.4, the kinetics of the K77 sensitized TiO$_2$ film indicates that the oxidized dye recombines with the electrons in TiO$_2$ conduction band on the time scale of hundred $\mu$s with half-time decay at 330 $\mu$s.$^{188}$ Even faster decay signal from K77$^+$ with half-time decay of 72 $\mu$s was observed when TPAA was employed as HTM, which indicates the efficient regeneration of K77$^+$ by TPAA in accordance with PIA measurement.

Moreover, the fast hole injection from K77$^+$ to TPAA was observed since the transient absorption signal from TPAA$^+$ was obtained only 100 ns after the excitation of K77, which indicates that the rate constant of hole injection is much greater than that of recombination between TPAA$^+$ and free electrons. Therefore the probed decay signal from K77$^+$ mainly corresponds to the charge recombination between TPAA$^+$ and the electrons in TiO$_2$ conduction band since the recombination reaction becomes the determining factor during the equilibrium. However, such a fast decay signal implies the fast
recombination between the charge-separated states, which significantly limits the device performance in spite of the efficient dye regeneration.

In agreement with TAS measurements, it was observed that the photocurrent remained low and the electron lifetime appeared to be fairly short due to the fast charge recombination. This is probably caused by that the TPAA molecules are located close to the TiO$_2$ surface inside the pores due to its small molecular structure facilitating the electron transfer reaction between the conduction band electrons and the holes in the TPAA layer. In order to solve this problem, as shown in Figure 5.5 a co-HTM strategy was proposed that the conjugated polymer P3HT with large bulky molecular structure and high conductivity was applied as co-HTM to transport the holes away from TPAA$^-$ to prohibit the recombination. The TAS decay signal was successfully delayed when P3HT was added as co-HTM to the K77/TPAA system (Figure 5.4), where the half-time decay was retarded from 72 $\mu$s to 290 $\mu$s indicating that the recombination is efficiently suppressed in accordance with the prolonged electron lifetime determined by photovoltage decay measurement.

Figure 5.5: Schematic energy level diagram of the sDSC device with co-HTMs of P3HT and TPAA, where the suggested charge transfer processes after light absorption of the dye is monitored.

As shown in the right panel of Figure 5.3, the PIA spectra of K77 sensitized mesoporous TiO$_2$ film with co-HTMs of TPAA and P3HT were also measured to further firm the efficient dye regeneration by the co-HTMs, where the sample was excited at 632 nm to avoid the absorption of P3HT. Due to the weak absorption of P3HT at this pump wavelength, the comparison between the PIA spectra of TiO$_2$/K77/TPAA and TiO$_2$/K77/(TPAA+P3HT) therefore confirms that the dye regeneration still remains highly efficient. In addition, the conductivity measurements were performed between two deposited Ag electrodes on the TiO$_2$/K77/TPAA and TiO$_2$/K77/(TPAA+P3HT) films. It was observed that under illumination the resistance in the device
with TPAA as HTM was reduced by a factor of 10 when P3HT was applied as co-HTM due to the reduced recombination and enhanced charge density.

In this paper the PIA and TAS measurements suggested that a small molecule organic HTM TPAA with excellent pore filling could be used to efficiently regenerate the oxidized dye molecules in sDSC devices. However, the photocurrent remains low and electron lifetime appears to be short due to fast charge recombination. Therefore the conducting polymer P3HT was applied as the co-HTM to suppress the recombination and to improve the hole conduction. With a small molecule HTM efficiently regenerating the dye molecules and a polymer HTM transporting the holes such a novel co-HTM design is therefore a promising strategy for the development of sMSCs.

5.3 The influence of ion migration on photovoltaic performance in sDSC (Paper III)

As discussed in previous chapters, the performance of spiro-OMeTAD based devices is limited by the incomplete pore filling and low hole-mobility. In order to overcome these limitations, with higher hole-mobility ($1 \cdot 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$) and solubility, MeO-TPD was studied as a cost-effective alternative HTM in combination with organic sensitizer LEG4 in sDSC.$^{152}$ In comparison, the sDSCs using MeO-TPD eventually provided higher IPCE and photocurrent, which reveals that an efficient infiltration of such a HTM into mesoporous TiO$_2$ electrode was achieved for efficient dye regeneration due to its relatively smaller molecular weight and therefore higher solubility in organic solvents.

The transient photovoltage and current decay measurements were performed to determine the electron lifetime $\tau_n$ and the response time of photocurrent decay $\tau_{\text{resp}}$, from which the electron transport time $\tau_{\text{trans}}$ was extracted according to Equation 4.13 showing that the charge transport in MeO-TPD based device is much faster than that of the device using spiro-OMeTAD as HTM. This is mainly attributed to the fact that the hole-mobility of MeO-TPD appears to be two orders of magnitude higher than that of spiro-OMeTAD, which therefore contributes to the higher effective diffusion coefficient of charge transport. The charge collection efficiency $\phi_{cc}$ was calculated based on $\tau_n$ and $\tau_{\text{trans}}$ according to Equation 2.7 indicating that MeO-TPD based devices harvest 19% more charges than spiro-OMeTAD based devices under 1 sun illumination. The faster charge transport together with higher $\phi_{cc}$ eventually enables MeO-TPD to outperform spiro-OMeTAD as alternative HTM in efficient sDSC devices.

It is worth noticing that an initial light soaking treatment at open circuit condition was found to be significantly essential for improving the photovoltaic performance of MeO-TPD based sDSC devices. As shown in Figure 5.6,
the device merely provided a low efficiency of 1.1% at its initial state after fabrication. However, by treating the devices under simulated 1 sun illumination (AM 1.5 G) at open-circuit condition for 30 minutes, the efficiency was surprisingly increased more than 4 times up to 4.9% following a bi-exponential curvature. Moreover, the power conversion efficiency remains impressively stable after the initial light soaking treatment with merely 0.2% drop over 580 hours when the unsealed devices were stored in the ambient atmosphere with low humidity (< 15%) at room temperature in the dark (Figure 5.6, inset).

![Figure 5.6: The evolution of power conversion efficiency $\eta$ of MeO-TPD based device fitted as a bi-exponential function of time under light soaking treatment at open circuit (AM 1.5 G, 1000 Wm$^{-2}$). The inset displays the fluctuation of $\eta$ over 580 hours after the initial light soaking treatment when the unsealed devices were stored in ambient atmosphere with low humidity at room temperature in the dark.]

In order to understand such an interesting phenomenon, electron lifetime was measured for MeO-TPD based devices before and after the initial light soaking treatment. It was observed that $\tau_n$ was significantly prolonged after the light soaking treatment indicating that charge recombination reactions were efficiently suppressed. Therefore the considerably low $V_{oc}$ and device efficiency exhibited before the light soaking treatment can be attributed to the fairly short $\tau_n$ due to the rapid charge recombination. It was well acknowledged that Li ions (Li$^+$) as additive are necessary for sDSC devices to function. This is partially attributed to that positively charged Li$^+$ ions tend to adsorb onto the negatively charged TiO$_2$ surface to compensate and screen conduction band electrons, which therefore prohibits charge recombination. Thus, a feasible hypothetic mechanism was proposed to interpret the observed phenomenon that Li$^+$ ions inside the pores tend to migrate towards TiO$_2$ surface due to the Coulombic interaction driven by the local electric
field induced after photo-excitation and charge separation at open circuit conditions.

Figure 5.7: The evolution of power conversion efficiencies as a function of time under light soaking treatment: the cell using MeO-TPD and t-BP (black trace with square), the cell using spiro-OMeTAD and t-BP (red trace with circle), on both devices a solution containing 1 M Li-TFSI was spin-coated on top of the complete devices after fabrication. Inset: the cell using MeO-TPD and t-BP without Li-TFSI (black trace with square), the cell using spiro-OMeTAD and t-BP without Li-TFSI (red trace with circle).

To verify the proposed hypothesis, complete sDSC devices with the same concentrations of HTMs and t-BP as used in the devices for I-V measurements were tested under the light soaking treatment in the absence of Li-TFSI. The device based on either MeO-TPD or spiro-OMeTAD exhibited negligible efficiency around 0.03% or 0.04%, respectively, independent on time during the light soaking treatment in the absence of Li-TFSI (Figure 5.7, inset). However, when the MeCN solution containing 1 M Li-TFSI was spin-coated on top, both devices exhibited the same evolution phenomenon in terms of efficiencies (Figure 5.7). This experiment clearly indicates that the evolution of device efficiency is caused by the presence of Li-TFSI dependent on time during the light soaking treatment. Moreover, to simulate the local electric field induced by charge separation under illumination at open circuit conditions, instead of light soaking a negative bias potential by 20 mV higher than $V_{oc}$ was applied in the dark across the device based on either MeO-TPD or spiro-OMeTAD with 1 M Li-TFSI solution spin-coated on top. As shown in Figure 5.8, the similar trends for the evolution of efficiencies as a function time were observed for both devices compared with the light soaking treatment, which clearly indicates that the essential driving force for Li$^+$ ion migration towards TiO$_2$ surface is the Coulombic interaction driven by the local electric field.
As shown in both light soaking and applied potential treatments, MeO-TPD based devices underwent much longer time to reach the optimal state than those based on spiro-OMeTAD where the time-dependent difference of Li$^+$ ion migration through HTM layer towards TiO$_2$ surface is due to the different nature of HTMs. The ion migration through MeO-TPD layer might suffer from higher steric hindrance caused by the stronger inter-molecular $\pi$-$\pi$ stacking due to its rigid planar molecular structure. In contrast faster ion migration can be expected through spiro-OMeTAD layer since the weak inter-molecular $\pi$-$\pi$ stacking in virtue of the twisted molecular conformation allows higher migration freedom with both intra- and inter-molecular pathways in three dimensions.

Moreover the light-soaking effect was found as a general observation in MeO-TPD based devices when the concentration of Li-TFSI is altered in a large range (Figure 5.9). Under light soaking treatment the device with higher Li$^+$ concentration provides better efficiency at its optimal state than those with lower Li$^+$ concentrations although it needs longer time to reach its optimal state for the majority of Li$^+$ migrating to TiO$_2$ surface. It was also observed that the evolution of device efficiency can be terminated and the efficiency can be maintained at the transient level when a positive bias potential equal to $V_{oc}$ was applied to prohibit the Li$^+$ migration to TiO$_2$ surface. These results indicate that Li$^+$ migration appears to be reversible and only driven by the local electric field, which therefore further verify the proposed mechanism for interpreting the light-soaking effect. Apart from MeO-TPD and spiro-OMeTAD, an impressive improvement of device efficiency
from 0.07% up to 1.5% was also observed in sDSCs using TPAA as HTM under light soaking treatment. The light-soaking effect in the presence of Li-TFSI seems to be rather general and is therefore considered to be of significant importance for the development of sDSCs based on different HTMs.

![Figure 5.9: The evolution of power conversion efficiencies fitted by bi-exponential function of time under light soaking treatment for the MeO-TPD based devices using a variation of Li-TFSI concentrations: 20 mM (black trace with square), 40 mM (red trace with circle), 76 mM (green trace with up-triangle) and 128 mM (blue trace with down-triangle).][1]

In this paper a small molecule organic HTM MeO-TPD was found to outperform spiro-OMeTAD in sDSCs in terms of faster charge transport and higher $\phi_{cc}$ due to its efficient pore filling and high hole-mobility. It was observed that an initial light soaking treatment at open circuit conditions significantly improved the electron lifetime and device performance. A mechanism of device performance evolution depending on Li$^+$ ion migration towards TiO$_2$ surface driven by the local electric field was suggested and verified. These results provide a promising pathway for the development of alternative HTMs in sDSCs.

5.4 PEDOT HTM prepared by *in-situ* PEP (Paper IV)

As shown in previous study (Paper I & II), the incomplete infiltration through the mesoporous electrode appears to be one of the major limitations on device performance in sDSCs when conjugated polymer are employed as HTMs. In order to solve such a problem, the *in-situ* photoelectrochemical polymerization (PEP) was developed. In this approach the polymerization based on radical coupling takes place inside the pores triggered by the process that photo-oxidized sensitizers inject holes into the small organic pre-
cursors (monomers) dissolved in surrounding electrolyte. Therefore high pore filling is generally achieved with polymer HTMs generated inside the pores by in-situ PEP. However, the organic solvents, typically MeCN, are usually employed as electrolyte to perform in-situ PEP due to the solubility limitation of monomers, which is unfavourable in terms of environmental concerns and large-scale production. In addition, the generally high oxidation potential of most monomers in organic media narrows the choice of applicable dye/monomer couples and may also cause overoxidation of materials in use. In order to avoid these problems, a novel method of performing in-situ PEP in aqueous micellar solution with bis-EDOT monomer (Figure 3.4) in combination with different sensitizers was developed based on the fact that aqueous media containing surfactants can efficiently dissolve most monomers meanwhile lower their oxidation potential.\textsuperscript{175-179}

The oxidation onset of bis-EDOT was reduced from 0.9 V to 0.6 V vs. SHE when MeCN was replaced by the aqueous micellar solution using TritonX-100 surfactant. The cross-sectional SEM images suggest that the high uniformity and pore filling of PEDOT were obtained due to the better surface organization of polymer deposited by aqueous-phase in-situ PEP. As shown in Figure 5.10, the device using aqueous-phase polymerized PEDOT provided 4.8\% efficiency competitive with 6\% from the device using PE- DOT produced by in-situ PEP from organic electrolyte.\textsuperscript{191} The slightly worse performance is attributed to the difference in the molecular and electronic structures of PEDOT produced from these two different electrolytes.

After the termination of in-situ PEP processes the deposited polymer usually remains doped in two forms, namely PEDOT\textsuperscript{+} (polaron) and PEDOT\textsuperscript{2+} (bipolaron), determined by its doping level. Since the optical property of conducting polymers is highly dependent on their doping states the presence of bipolaron state with higher doping level can be identified by its broad absorption in the near-IR spectral region.\textsuperscript{192} According to the results of near-IR absorption spectra (from 780 nm to 1700 nm) and the space charge limited current measurements (SCLC) published in the relevant studies,\textsuperscript{193,194} the aqueous-phase polymerized PEDOT exhibits a weak absorption band in near-IR region while a considerably stronger band covering the entire observation spectral range was measured for the organic-phase polymerized PE- DOT. This indicates that the electronic structure of the aqueous-phase polymerized PEDOT shows a spectral feature with main contribution from polaron state corresponding to a less delocalized conjugated molecular structure with shorter polymer chain length while the doping state of the organic-phase polymerized PEDOT exhibits a spectral feature mainly attributed to bipolaron probably due to a highly delocalized conjugated molecular structure with longer polymer chain length.\textsuperscript{192} Such a subtle difference in the molecular and electronic structures of PEDOT is caused by the slightly different mechanism during in-situ PEP processes. According to the mechanism of radical polymerization, the local concentration of active free radicals inside the pores remains high in organic electrolyte facilitating the continuous
polymerization within a long time domain and therefore longer polymer chain length while it is limited by micelles in aqueous solution leading to faster termination of polymerization and therefore shorter polymer chain length.

Figure 5.10: $I-V$ characteristics of sDSCs: the devices using organic-phase polymerized PEDOT as HTM in combination with LEG4 (red trace with circle) or Z907 (blue trace with square) as sensitizer; the device using aqueous-phase polymerized PEDOT as HTM in combination with LEG4 as sensitizer (black trace with diamond).  

In addition, the hole-mobility of PEDOT was determined by SCLC according to Equation 4.3 in these studies.  

It was observed that the aqueous-phase polymerized PEDOT shows a much lower hole-mobility of $1.25 \cdot 10^{-5} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ than those measured for the organic-phase polymerized PEDOT. These data is in agreement with the interpretation of near-IR absorption spectra since the hole-mobility increases when the charges are more delocalized in larger conjugated structures. Therefore it can be assumed that the hole transport proceeds faster in the PEDOT layer deposited from organic electrolyte.

In this paper, a novel method to perform in-situ PEP in the aqueous micellar solution of $bis$-EDOT monomer was developed to cope with the infiltration difficulty of polymer HTMs in sDSCs. The device showed impressively high performance as competitive as those using PEDOT produced from organic electrolyte. Therefore the development of in-situ PEP in aqueous micellar electrolyte provides an environmental-friendly alternative pathway with scale-up potential for constructing efficient sDSCs with conjugated polymers as HTM. According to the results of near-IR absorption spectra and hole-mobility measurements published in the relevant extensive study based on the present paper, the different device performance based on PE-
DOT deposited by \textit{in-situ} PEP from either aqueous or organic electrolyte can be interpreted by that with higher doping state organic-phase polymerized PEDOT exhibits a greater hole-mobility due to its highly delocalized conjugated molecular structure with longer polymer chain length.

5.5 The influence of different HTMs on perovskite based sMSC (Paper V)

Due to its highly efficient light harvesting, the CH$_3$NH$_3$PbI$_3$ perovskite based sMSC has become a promising photovoltaic device for energy conversion. Although the device structure appears to be quite similar with sDSC, as an emerging technology the influence of HTM on device performance remain poorly understood. In this paper three different HTMs (DEH (Figure 3.2), spiro-OMeTAD and P3HT) in terms of molecular structure and properties were used to investigate the influence of HTM on the regeneration and charge collection efficiencies in the CH$_3$NH$_3$PbI$_3$ perovskite based sMSC devices.

![Figure 5.11: I-V characteristics of CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs using DEH, spiro-OMeTAD and P3HT as HTM respectively, where Li-TFSI and \( t \)-BP were employed as additives in all cases.\textsuperscript{159}](image)

As shown in Figure 5.11, the CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs using spiro-OMeTAD, P3HT and DEH as HTM provided the energy conversion efficiency of 8.5%, 4.5% and 1.6% respectively, where the difference was attributed to the different photocurrent, voltage and fill factor.\textsuperscript{159} The IPCE spectra indicate that the light absorption of HTM was negligible and the trend of difference in IPCE and photocurrent were in accordance to that observed in \( I-V \) characterization following the sequence \( J_{\text{spiro-OMeTAD}} > J_{\text{P3HT}} > J_{\text{DEH}} \). Moreover the photocurrent of these devices was found to be linearly
dependent on the incident light intensity, according to Equation 4.7 which therefore indicates that the IPCE appears to be constant independent on the photon flux. Since the LHE of these devices is constant and similar, the APCE of these devices is therefore also independent on the light intensity subject to the same trend of difference as observed for photocurrent.

The results of PIA measurements suggest that these three HTMs all regenerate the oxidized perovskite in efficient manner probably due to the sufficient regeneration driving force between the HOMO level of HTM and the VB edge of perovskite. According to Equation 4.8, therefore the charge collection efficiencies (\(\phi_{cc}\)) of these devices also seem to be independent on the light intensity and follow the same trend of difference as observed for photocurrent and IPCE.

The difference in \(\phi_{cc}\) of these devices is probably derived from the large difference in the electron lifetime (\(\tau_n\)). The transient photovoltage decay measurements were performed to extract the electron lifetime. The Figure 5.12 shows the measured \(\tau_n\) as a function of \(V_{oc}\) (at different light intensities), where the decrease in \(\tau_n\) at higher light intensity or \(V_{oc}\) is attributed to the faster recombination as the result of the increased charge density of conduction band electrons. Moreover, it is clearly shown that the electron lifetime of these devices using three different HTMs decreases by one order of magnitude in the sequence \(\tau_{\text{spiro-OMeTAD}} > \tau_{\text{P3HT}} > \tau_{\text{DEH}}\) indicating that the rate constants of the recombination reactions follow the reverse sequence.

The Marcus theory suggests that the kinetics of electron transfer reactions is determined by the energetic driving force and the electronic coupling between the two transition states. Therefore the recombination rate constants of these devices are dependent on the difference between the HOMO level of
HTM and the VB edge of perovskite and the electronic and geometrical structures of the HTM and perovskite. The former was verified to be sufficient enough by PIA and electrochemical measurements while the latter highly depends on the nature of the HTMs. The relatively bulky molecular structure of spiro-OMeTAD with twisted centre of spiro-carbon introduces steric hindrance to partially protect the TiO$_2$ and perovskite surface away from spiro-OMeTAD in its oxidized form, which therefore lowers the probability of recombination and prolong the $\tau_n$. While the DEH might be located much closer to the TiO$_2$ and perovskite surface due to its small and planar structure resulting in faster recombination and shorter $\tau_n$. In contrast, in spite of the high hole-mobility of up to 0.1 cm$^2$V$^{-1}$s$^{-1}$, the pore filling issue of P3HT may lead to the incomplete regeneration of the oxidized perovskite. However, the PIA spectra show that the regeneration may be rather efficient also for P3HT possibly due to high hole mobility in the perovskite layer. Instead large recombination probability of holes in the P3HT with the conduction band electrons in the TiO$_2$ or perovskite, due to close contact between the polymer and the TiO$_2$ or perovskite might limit the performance. Thus, the different device performance of the CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs using spiro-OMeTAD, P3HT and DEH as HTM is mainly attributed to the difference in charge recombination reactions.

In this paper, three different types of HTMs (DEH, spiro-OMeTAD and P3HT) were employed to investigate the influence of HTMs on the regeneration and charge recombination reactions in CH$_3$NH$_3$PbI$_3$ based sMSC devices. It was observed that the electron lifetime ($\tau_n$) of these devices using three different HTMs decreases by one order of magnitude in the sequence $\tau_{\text{spiro-OMeTAD}} > \tau_{\text{P3HT}} > \tau_{\text{DEH}}$. Therefore it was concluded that the photovoltaic performance of the CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs highly depends on the nature of the HTMs in terms of charge recombination reactions.
6. Conclusions and outlook

During the past two decades the solid-state mesoscopic solar cells (sMSCs) have been developed as a promising alternative technology to the conventional photovoltaics. However, there are still several limitations constraining the device performance, such as the incomplete infiltration of the hole transport materials (HTM) into the mesoporous electrodes and the relatively low hole-mobilities of the most commonly used HTMs. There are two types of sMSCs included in the study of this doctoral thesis, namely solid-sate dye-sensitized solar cells and organometallic halide perovskite based solar cells. Based on the investigation of the fundamental operating mechanisms of the different HTMs in sMSCs to identify the limiting factors in these devices, a variety of HTMs and different preparation methods have been studied in order to circumvent these limitations and to further improve their photovoltaic performance.

To investigate the influence of HTMs on sDSC performance in terms of hole-mobility and pore filling, two different types of HTMs, namely the small molecule organic HTM spiro-OMeTAD and the conjugated polymer HTM P3HT, were studied in combination with two organic sensizers D35 and M3. The photo-induced absorption spectroscopy (PIA) spectra in association with spectroelectrochemical data suggested that insufficient regeneration of oxidized dye species was observed in P3HT based devices. According to the results of PIA and the scanning electron microscopy (SEM), compared to spiro-OMeTAD less sufficient pore filling of P3HT into the mesoporous electrode was identified as the primary reason for their worse device performance. Moreover, it was noticed that the dye-dye hole conduction occurs in the absence of HTM and appears to be more efficient through the dye layer of D35 than M3 rationalizing the better performance of D35 over M3 in P3HT based devices. Therefore the hole diffusion length through the monolayer of sensitizers by dye-dye hole conduction could be of significant importance to the contribution of hole transport, which is realized to be crucial for optimizing such a hybrid system with conjugated polymers as HTM (Paper I).

In order to cope with the problems of incomplete pore filling and low hole-mobility, a small molecule organic HTM TPAA with high solubility and hole-mobility was employed as HTM in sDSCs. The results of the transient absorption spectroscopy (TAS) and PIA measurements suggested that the regeneration of oxidized dye was highly efficient due to the excellent pore filling of TPAA. However, the device performance remains low suffering
from the fast recombination indicated by the short electron lifetime. Therefore the conducting polymer P3HT was applied as the co-HTM to transfer the holes away from TPAA, which successfully removes the charge density of holes away from the TiO₂ surface for suppressing the recombination and improving the hole conduction. Thus, the novel co-HTM design is a promising strategy for the development of sMSCs by using a small molecule HTM regenerating the oxidized dye molecules and a polymer HTM transporting the holes (Paper II).

Based on the high solubility and hole-mobility, an alternative small molecule organic HTM MeO-TPD was found to outperform spiro-OMeTAD in sDSCs. The faster charge transport and higher $\varphi_{cc}$ were achieved in MeO-TPD based devices due to its more efficient pore filling and higher hole-mobility. Moreover, it was observed that the device efficiency increases as a bi-exponential function of time and the electron lifetime was significantly improved under light soaking treatment at open circuit conditions. In order to interpret such an interesting phenomenon, a light soaking treatment and an applied potential treatment were performed on these devices with or without Li-TFSI. According to the results, a mechanism of device performance evolution depending on Li$^+$ ion migration towards the TiO₂ surface driven by a local electric field was suggested and verified. Such a mechanism of Li$^+$ ion migration is therefore of significant importance for the development of alternative HTMs in sDSCs (Paper III).

In order to overcome the difficulty of thoroughly infiltrating conjugated polymer HTMs through the mesoporous electrode, a state-of-the-art method to perform in-situ photoelectrochemical polymerization (PEP) in the aqueous micellar solution of bis-EDOT monomer was developed as an environmental-friendly alternative pathway with scale-up potential for constructing efficient sDSCs with polymer HTMs. The device exhibited competitive performances as those using PEDOT produced from organic electrolyte. The results of near-IR absorption spectra and hole-mobility measurements published in the relevant extensive studies indicate that the chemical and electronic structures of PEDOT deposited by in-situ PEP highly depend on the polymerization mechanism in either aqueous or organic electrolyte. In general, it was concluded that with higher doping state organic-phase polymerized PEDOT exhibits a greater hole-mobility due to its highly delocalized conjugated molecular structure with longer polymer chain length (Paper IV).

To investigate the influence of HTMs on the regeneration and charge recombination reactions in CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs, three different types of HTMs, namely DEH, spiro-OMeTAD and P3HT, were studied. The PIA in combination with electrochemical measurements suggests that the regeneration of oxidized perovskite appears to be efficient by these three HTMs with sufficient energetic driving force. The photovoltage decay measurements indicate that the electron lifetime ($\tau_{el}$) of these devices using three different HTMs decreases by one order of magnitude in the sequence
It was therefore concluded that the photovoltaic performance of the CH$_3$NH$_3$PbI$_3$ perovskite based sMSCs highly depends on the charge recombination reactions according to the nature of the HTMs, which provides an insight for developing novel HTMs for the perovskite based sMSCs in future (Paper V).

For future work, in order to improve the photovoltaic performance of sMSCs it would be interesting to develop novel small molecule organic p-type semiconducting materials as HTMs featuring low cost, high chemical and photo-stability, high solubility, low melting point, high hole-mobility and efficient pore filling into mesoporous electrodes. Alternatively, it would also be interesting to develop novel methods to efficiently infiltrate the HTMs into sMSCs, such as the melt-infiltrating techniques and the in-situ PEP with novel applicable sensitizer/monomer couples.
Sammanfattning på svenska

Inledning

Energi och miljö har blivit två av de viktigaste områdena under de senaste åren. Den mänskliga civilisationen har nått stora framgångar i och med industrialiseringen men det har varit på bekostnad av förbrukning av icke-förnyelsebara energikällor och globala klimatförändringar. Detta medför en rad olika hinder mot en hållbar utveckling för kommande generationer. Den totala globala energianvändningen har ökat snabbt under de senaste årtiondena och nått ett slående rekord av 8919 Mtoe (miljoner ton oljeekvivalenter) under år 2011.\(^1\) Användningen av icke förnyelsebara energikällor står fortfarande för den största delen av energiproduktionen med ungefär 66.4%, vilket inkluderar råolja, kol och naturgas. Förbränningen av fossila bränslen har orsakat oåterkalleliga miljöskador, såsom luftförvärrningar och global uppvärmning. För att klara dessa framtida utmaningar är forskning inom teknik och förnyelsebar energi nyckeln till en hållbar framtid. Solenergi anses vara den enda "outtömliga" energikälla som finns. Solen förser jordens atmosfär med en effekt av ungefär 1.7 \(\times\) \(10^5\) TW elektromagnetisk strålning. Detta motsvarar ca 600 TW på marken enligt en genomsnittlig solinstrålning mot jorden på 1367 W per kvadratmeter och omkring 30% reflektion mot jordatmosfären. Ungefär 1 \(\times\) \(10^9\) TWh solenergi träffar atmosfären under ett år och jämförs med den nuvarande globala energiförbrukningen, under 2011 som uppskattades till drygt 19 000 TWh.\(^2\) är solenergin som träffar jorden betydligt mer än det som krävs för att fullt ut täcka elbehovet i världen. Som förnyelsebar energiteknik har solceller visat stor potential med anmärkningssvårt snabb tillväxt under det senaste decenniet. Fram till början av 2014 har en total kapacitet på cirka 139 GW installerats runt om i världen. Trots den stora ökningen av solcellsinstallationer förblir utmaningen att minimera återbetalningsstid och tillverkningskostnad. För att ge tillräckligt bidrag till världens elproduktion för hållbar utveckling, behöver fler och mer högeffektiva, kostnadseffektiva, återvinningsbara och miljövänliga solcellssystem utvecklas i framtiden.\(^5\)

Färgämnes-sensitiserade solceller

Konceptet färgämnes-sensitering (infärning) introducerades ursprungligen av Moser med flera under sent 1800-tal som visade att ljuskänsligheten i
fotografisk film blev bättre genom färgämnes-sensitering av halogenerat silver (Ag).\textsuperscript{14} Intensiv forskning om färgämnes-sensitiserade solceller (Dye-sensitized Solar Cell, DSC) har bedrivits sedan en billig fotoelektrokemisk cell med 7% verkningsgrad demonstrerades av O'Regan och Grätzel under 1991.\textsuperscript{16} Genombrottet berodde på en kombination av en mesoporös titandi-oxidfilm (TiO\textsubscript{2}), som används som fotoanodmaterial, färgämnesmolekyler på denna elektrod och en elektrolyt som innehöll redox paret jodid/trijodid. Färgämnes-sensitiserade solceller tillverkas mestadels av material som vanligvis är kostnadseffektiva och miljövänliga. Såsom visas i Figur 1, utgörs fotoanoden av ett lager av nanopartiklar av ett n-typ halvledarmaterial, t ex, anatas TiO\textsubscript{2} (i allmänhet med nanopartiklar med omkring 20 nm i diameter) på fluordopad tenndioxid FTO (F:SnO\textsubscript{2}) belagt på glas. Fotoanoden beläggs med ett lager av färgämnesmolekyler (färgämnes-sensitering). En elektronsnisk övergång sker vid ljusabsorption hos färgämnesmolekylerna, vilket leder till bildning av ett exciterat tillstånd hos färgämnet. Excitationen leder till injektion av en elektron från färgämnet till nanopartikeln. De injicerade elektronerna transporterar efteråt genom det sammankopplade mesoporösa TiO\textsubscript{2} nätverket mot FTO substratet och transporten beskrivs av en diffusionsprocess.\textsuperscript{18,19} Efter elektroninjektion är färgämnesmolekylen i oxiderad form och regenereras genom elektrondonation från elektrolyten innehållande I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-} redoxparet upplöst i ett organiskt lösningsmedel. Den positiva laddningen överförs via redoxparet till den platinerade FTO motivelektroden för att slutföra kretsen.\textsuperscript{20,21}

Spänningen som man får ut av en DSC bestäms av energiskillnaden mellan redoxpotentialen hos elektrolyten och elektron kvasi-Ferminivån (E\textsubscript{F}) i TiO\textsubscript{2} under arbetsförhållanden (i solljus och med en viss ström och spänning). Den fotoström som kommer från solcellen beror på absorptionsspektrum av
färgämnet och absorberad foton till strömomvandlingseffektivitet, vilken beror på den interna kvanteffektiviteten. Under de senaste två decennierna har forskningsinsatser ägnats åt att förbättra solcellsprestandan. Världsrekordverkningsgraden på 13% för DSCs baserad på vätske-elektrolyt, erhölls av Grätzel med flera under 2014. Den solida färgämnens-sensitiserade solcellen (sDSC) är en typ av solida mesoskopiska solceller (sMSC), och har utvecklats för att ersätta den flytande elektrolyten med en solid halvledare (håltransportmaterial, HTM). Genombrottet för sDSC demonstrerades framgångsrikt av Bach med flera i 1998 genom att använda en liten organisk p-typ halvledarmolekyl, 2,2’,7,7’-tetrakis(N,N-dimethoxyphenylamine)-9,9’-spirobifluorene, benämnd som spiro-OMeTAD (Figur 2) som HTM vilket ersatte den konventionella flytande elektrolyten. Sedan dess har intensiva forskningsinsatser ägnats åt sDSC. Effektiviteten hos sDSC med spiro-OMeTAD som HTM tillsammans med ett organiskt färgämne har förbättrats markant till 6.08% för en certifierad solcell, och senare till 7.2% genom tillsats av ett koboltkomplex som p-typ dopämne.

Perovskit-baserade solceller

Utifrån kunskapen om metallorganiska halidperovskiter som förvärvats i forskningområden om lysdioder och transistorer, kom idén att använda metallorganiska blyhalogenidperovskiter som ljusfångare (färgämne) i elektrolytbasierade fotoelektrokemiska solceller (färgämnessolceller) och introducerades av Miyasaka med flera 2009 med en verkningsgrad på 3.8%. På grund av upplösningen av perovskiten i de organiska elektrolyten minskade effektiviteten hos solcellen snabbt efter det att solcellen tillverkats även om en verkningsgrad på som bäst 6.5% erhölls. Genom att ersätta elektrolyten med det solida håltransportmaterialet spiro-OMeTAD kunde en signifikant förbättring till 9.7% effektivitet uppnås av Park med flera under 2012. Vid ungefär samma tidpunkt, visade Snaith med flera framgångsrikt att TiO₂ fotoanoden även kan ersättas av isolerande mesoporös Al₂O₃ vilket gav en
verkningsgrad på 10.9%, i en metallorganisk blyhalogenid perovskit baserad sMSC. De vanligaste blyhalogenid perovskiterna i sMSC är formulerade som CH₃NH₃PbI₃ och CH₃NH₃PbI₃₋ₓClₓ på grund av skillnaden i framställningsmetoder. Möjligheten att modifiera molekylformel och struktur med substitution av övergångsmetaller och ändra halid-sammansättning, ger en mängd olika möjligheter för att förbättra solcellernas prestanda. Hittills har ett imponerande världsrekord på 17.9% uppnåtts för denna typ av solceller.

Förbättringar i mesoskopiska solceller

Att förändra de inneboende egenskaperna hos háltransport materialet t.ex. spiro-OMeTAD är en viktig faktor för att förbättra den relativt låga effektiviteten i sMCSs, jämfört med vätske-baserad elektrolyt DSCs. Exempelvis låg laddningsmobilitet, snabb rekombinationshastighet och otillräcklig infiltra

Förbättringar i mesoskopiska solceller

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